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THE BINAURAL LOCATION
OF COMPLEX SOUNDS

BY

R. V. L. HARTLEY and THORNTON C. FRY

A DISCUSSION
OF THE BINAURAL LOCATION OF COMPLEX SOUNDS
BASED ON THE THEORIES DEVELOPED FOR PURE TONES

The Binaural Location of Complex Sounds

By R. V. L. HARTLEY and THORNTON C. FRY

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NOTE: Much has been written on the subject of the binaural location
of pure tones but the case of complex sounds has received little attention
in recent literature. The purpose of the present paper is to bring the dis-
cussion of complex sounds abreast of that relating to pure tones. Those
who wish to acquaint themselves with the work on pure tones will be inter-
ested in reading the theoretical work of the authors and the experimental
studies carried out by G. W. Stewart and students working under his
direction. This work has been reported in various papers, most of which
have appeared during recent years in the *Physical Review* and the *Physi-
kalische Zeitschrift.*

A résumé of the present paper is given by the authors in their concluding
paragraph.

THE need of determining the location of enemy submarines and
aeroplanes during the war brought into use practical methods
for locating a sound source which depend upon differences between
the sound waves reaching the two ears. This stimulated a general
study of the phenomena involved in binaural sound location. The
foundation for this study had already been laid in the work of Lord
Rayleigh and others, who, following more or less in his footsteps,
had accumulated a considerable amount of information of both
theoretical and experimental sorts. Of this information almost all
that was of a theoretical nature and a considerable portion of the
experimental kind dealt only with the location of *pure* tones, the more
complicated and in some respects more important problem of *complex*
sounds being almost entirely neglected. Such advances as were
made in the theoretical aspects of the problem during the war were
subject to the same restrictions so that even to-day no comprehensive
theory has been advanced which adequately covers the problem of
the location of such sounds as occur in everyday life, and in the
practical applications of binaural methods. However, the results
obtained with pure tones can be made to throw considerable light
upon the problem, and it is primarily from this standpoint that the
following discussion is written.

It may be well at the outset to review some of the outstanding
differences between the observed phenomena in the two cases. The
accuracy of location is much less for pure tones, as is also the sense
of definiteness of the sound image. The location of pure tones is almost
wholly binaural, as is evidenced by the inability of persons deaf in one
ear to locate such a tone. With complex sounds not only is the
location by binaural effects more accurate and definite, but also the
observer is not dependent on these alone. Persons who are deaf

in one ear can locate familiar complex sounds almost as well as those
with normal hearing.

Practically all theories of sound location start from the assumption
that the listener subconsciously observes certain sound characteris-
tics which depend upon the position of the source and forms a judg-
ment of where the source must be by comparing these characteristics
with information which he has stored up as a result of his past ex-
perience with cases in which the position of the source was known.
In order to fix the position of the source he must assign to it three
coördinates, such as its distance and some two angles which define
its direction. To do this he must be able to observe at least three
independent properties of the sound which are functions of the posi-
tion of the source. If fewer than three are available some difficulty
in location is certain to arise. If more than three are available there
is the possibility of a number of simultaneous independent determina-
tions of the three coördinates.

If the sounds of everyday life were never distorted in transmission
all of these determinations would yield the same set of coördinates
and the only advantage which the listener would gain from the addi-
tional information available would lie in the fact that some one set
might be peculiarly sensitive to slight differences in the position
of the source, and therefore might lead to increased certainty on the
part of the observer. Owing to reflection from the walls of buildings
and the like, the sounds of everyday life seldom arrive undistorted,
so that the observer must always be somewhat uncertain as to whether
or not the coördinates of the sound source are actually those which
he deduces from the properties of the sound wave as it reaches his
ears. If enough properties are available to permit him to make
two independent determinations he may use one of them to check the
other, and if they agree he is justified in a feeling of increased cer-
tainty as to the accuracy of his judgment. The more independent
determinations he can make, the more checks he will be able to apply
and consequently the more confident he will be.[1]

It should not be inferred, however, that it is only the sounds of
the street which reach the observer in a distorted form. In a great
many laboratory experiments the characteristics of the sounds have

[1]It is interesting to note in this connection that it is not surprising that an observer
locates a complex tone with much greater certainty than a pure tone when we con-
sider how rapidly the number of independent sets of data increases with increase
in complexity of sound. We have already said that three independent properties
are needed for the determination of the three coördinates of the source. Hence
if only three are available, only one determination can be made and no checks are
possible. On the other hand, if four are available, four groups of three each can
be formed and therefore four separate determinations can be made. Similarly,
10 determinations can be made from 5 properties, 20 from 6, and 120 from 10.

been inconsistent, and in some cases they have not even corresponded to any actual source whatever. Under these circumstances, if an image is formed at all, some purely psychological factors must enter in. For pure tones it has been found possible to explain much of the experimental data obtained under circumstances such as this by assuming that the observer subconsciously judges one or more of the characteristics to be in error and applies such corrections as will make all of the data correspond to an actual source. As a criterion for determining which characteristics will be altered, it is assumed that, in general, those are chosen which require the smallest changes.

Let us now consider what characteristics are available for locating sounds of different kinds. A pure tone from a source at rest with respect to the observer has at any point only two physical character-istics which are subject to change with the position of the source. They are its amplitude and phase. Corresponding to each position of the source there is a particular amplitude and phase at each of the two ears so that a total of four properties—the loudness of the sound, the average phase, the difference in amplitude (which may conven-iently be expressed as a ratio) and the difference in phase at the two ears—are available for determining the position of the source. It is inconceivable that the average phase can have anything to do with the location of the sound, since it may be changed at will without altering the position of the source. The same remark applies to the loudness of the sound except in those instances where the observer is familiar with the source to such an extent as to know how loud it may be expected to be. Hence if we restrict ourselves to the cases in which prejudicial information of this sort does not exist, we find that the observer has only two quantities from which he may deduce the position of the source. We should therefore expect that these two quantities would make it possible to locate the tone with respect to two coördinates only. This is found to be in general agreement with experiment, for most observers locate all sources of pure tones in the same horizontal plane with their heads and determine only the distance and angular departure from the median plane. If the source is more than a few yards away the intensity ratio and phase difference change very slowly with distance so that in this case even the sense of distance is not keen and a feeling of certainty exists with respect to the direction only.

In many experiments the tones at the two ears have been varied arbitrarily so as to give combinations having equal phases and un-equal intensities or vice versa—combinations which cannot arise from actual physical sources in the absence of distortion. Under

these conditions the observer generally corrects one to a value consistent with the other except in extreme cases where the correction required for this purpose would be inordinately large. When this occurs he may either assume both to be correct and form two images—one based on the phase difference together with a mentally supplied intensity ratio consistent with it, and the other similarly derived from the observed intensity ratio—or he may fail to have a sense of location at all.

Before considering the available characteristics of complex sounds in general let us confine our attention for a time to those which are made up of a limited number of sustained pure tones, such as an organ note with its series of overtones, or a group of tuning forks. Here the number of characteristics increases rapidly with the number of component tones. For each component tone there are two quantities: intensity ratio and phase difference. In addition, at either ear alone the relative intensities of any two of the tones changes with the position of the source, owing to the diffraction of the sound waves around the head being different for different frequencies. There are therefore as many of these observable intensity ratios as there are pairs of components. Similarly, for any two tones whose frequencies are commensurable, the relative phases of the two at the same ear depend upon the position of the source.

Not all of these characteristics are capable of contributing to binaural as distinct from monaural location. In fact, only the phase differences and intensity ratios of the separate components are binaural. A man who is deaf in one ear has available all of the relations between the intensities and phases of the various components at his normal ear. That these relations do actually contribute to sound location is supported by experimental evidence. Myers[2] found that, after familiarizing himself with a complex sound, a blindfolded observer could locate its position with considerable accuracy, even when it was moved about in the median plane, but that his accuracy could be destroyed by varying the relative intensities of the components.[3] It is not surprising, then, that for complex sounds the accuracy is about the same whether the location is binaural or monaural.[4] The observed failure of monaural location in the case of a

[2] C. S. Myers, *Proc. Royal Soc.*, 1914, B 88,267.

[3] It should be noticed that this effect must have been purely psychological, since it could be produced without moving the source at all. It therefore lends plausibility to the assumption upon which our theory is based: that when discordant or unusual stimuli are experienced, a mental readjustment of the stimuli is made in order to render them more nearly consistent with everyday experience.

[4] As shown by the experiments of Angell and Fite upon persons deaf in one ear. *Psychol. Rev.*, vol. 8, pp. 225-246, 1911.

pure tone follows directly from the absence of other frequencies with which the pure tone may be compared.

As we are here concerned with binaural phenomena we shall confine our attention to the relative phases and intensities at the two ears. The question at once arises: Does the observer actually hear the different tones separately, and if so, does he assign a location to each separately?

To what extent the listener locates each component separately depends upon the ease with which the tones can be distinguished. The experiments which bear most directly upon this point are those in which the component tones at the two ears are arbitrarily adjusted to give values of phase difference corresponding to different locations. This is done under conditions where the location of each component separately is largely determined by the phase difference. More[1] experimented with two tones, transmitting them to the ears through tubes of adjustable lengths. This permitted him to change the phase difference at the two ears while keeping the intensities substantially equal. He observed the apparent location for various settings when each tone was applied by itself and when both were applied together, using forks of 256 and 320 cycles. With the paths equal, the tones combined into a chord located in the median plane and the separate components could not be heard. With a setting for which the two components separately appeared on opposite sides of the head, one component was heard distinctly by the right ear only on the right side, and the other by the left ear only on the left side. At the same time the chord was heard rather indistinctly near the median plane but tending slightly toward the side of the lower tone.

Apparently the observer does not consciously separate the chord into its components unless he is forced to do so by some inordinate discrepancy between the positions of the images formed from them. There is no evidence in the case of equal paths to show that he did or did not subconsciously locate the separate components and find them to be in agreement. In view of the second experiment it seems probable that he did. In this latter experiment he obviously found that the two components corresponded to different locations and assigned different sources to each. At the same time his experience told him that tones which would combine to form a musical sound generally have a common source. Hence he may have concluded subconsciously that the sound waves had probably been distorted in coming from a common source and so he corrected his observations

[1]Louis T. More: *Phil. Mag.* XVIII, 1909, p. 308.

on both tones to make them consistent and arrived at an image of the chord between the other two.

Similar results were obtained with forks of 256 and 384 cycles per second, except that in general the lower tone was completely blotted out. The higher tone was usually quite distinct and definitely located. The image of the chord was nearer to the image formed when the higher component was sounded by itself than to the image formed from the lower one alone. With settings for which the directions of the tones separately were the same, whether right, left, or middle, the upper tone disappeared, leaving only the chord. In experiments with forks of 256 and 512 cycles it was difficult to distinguish the separate notes. With settings for which the two separately were on opposite sides the combination was on the side of the lower fork. This can be interpreted as meaning that the octave relationship is inherently difficult to resolve, or else that tones an octave apart so generally come from a common source that the observer was unwilling to make any other assumption.

Although the explanation of these results is not yet thoroughly understood, they show very definitely that in locating complex sounds made up of pure tones the observer does within limits locate the components separately. If they agree, a single image is formed; if they do not, he may either locate the tones separately or form a single compromise image, or do both.

It is in this way that the theory developed for pure tones is applied to complex sounds made up of pure tones. The next step is to extend it so as to include complex sounds in general. To do this we must picture the observer as resolving each sound into sinusoidal components, locating the components separately and forming one or more images based on a combination of the apparent sources as indicated by the separate components. While it is fairly easy to effect such a resolution mathematically it is somewhat less easy to interpret the result in a manner satisfactory to our intuitive conceptions of the phenomena involved; also, granted the theoretical possibility of the resolution, there remains the question of what physical or psychological limitations there may be to its application.

In view of the fact that a really pure component tone has no beginning or end, and no fluctuations in its amplitude, it is not at once apparent how a single discrete sound, such as the bark of a dog, can be resolved into components of that nature. However, if enough components are available, it has been established beyond question that by properly choosing their frequencies, amplitudes, and phases, a

combination may be arrived at in which the algebraic sum of all the components is zero for all instants before and after the period occupied by the sound and equal to the instantaneous value of the sound wave for instants within that period. This combination is known to mathematicians as the Fourier Integral corresponding to the wave, and the formula for the phase and amplitude of each component sinusoid is known. It is an extension of the well known Fourier series expansion used for resolving sustained periodic disturbances.

The physical interpretation of this integral may be facilitated by reviewing the steps in its evolution from the Fourier series. It is well known that if the sound in question were repeated at regular intervals the resulting periodic wave could be resolved by Fourier analysis into a series of sinusoidal components, the frequencies of all of which are integral multiples of the frequency of repetition of the sound. Successive components therefore differ in frequency by an amount equal to this frequency of repetition. Now it is not essential that the repetitions of the sound follow each other immediately. Instead, they may be separated by intervals of silence. The effect of such silent intervals is to reduce the frequency of repetition and therefore also the fundamental frequency. As a result the component frequencies are brought closer together and the number within any particular frequency range is increased.

Suppose, now, that the interval between repetitions is indefinitely increased. As this is done the effect of any one occurrence of the sound becomes more and more independent of the others, and in the limit when the sounds next preceding and next following the one under consideration are infinitely far removed, we have the case of a discrete sound. As this limiting case is approached the fundamental frequency becomes smaller and smaller and the component frequencies, which are multiples of it, are separated by infinitesimal frequency differences. While the amplitude of each component also decreases, the number of components increases at such a rate that the aggregate energy of all the components within a given frequency range remains finite. In this way the distribution of the sound energy over various frequencies—that is, the "energy spectrum"—can be obtained.

It is evident, then, that when an aperiodic complex sound is resolved mathematically there results an infinity of component tones, each having a characteristic intensity and phase. If an observer were capable of an equally complete resolution he would have at his disposal an infinity of sets of data from which an infinity of images could be formed. In the absence of distortion these should all coincide.

7

Practically, of course, no such refinement of resolution is possible. The ability to distinguish differences in pitch varies from person to person, but the minimum intervals employed in musical composition probably give a rough measure of the normal resolving power of the ear. Even with this limitation the broad sound spectrum, such as an irregular sound produces, is capable of yielding a very large number of separable components; and hence a large number of individual images. It is this fact—that with a very complex sound the number of independent determinations of the image is limited only by the resolving power of the observer—which makes his accuracy of binaural location as well as his sense of certainty much greater for such sounds than for pure tones.

So long as the images of all the components coincide, it is of little importance how fine the resolution is, for further refinement only serves to increase the sense of certainty by adding to the volume of accordant evidence. However, when the images are not in agreement the problem is more complicated and the degree of resolution becomes important. Here also purely physical considerations cease to be adequate and psychological factors must be considered similar to those involved in the location of a pure tone for which the intensity ratio and phase difference do not correspond to any actual source. When an observer is faced with discordant results he must make some subconscious judgment. For small discrepancies such as occur in everyday experience, he probably assumes those images which depart most from the rest to be misplaced because of distortion during transmission and so either corrects or ignores them. If the discrepancies are large he may find it difficult on the ground of experience to believe that so much distortion could occur. In such an event he will most likely form several images from different components or in extreme cases lose the sense of location altogether.

Bowlker found separate images to occur experimentally both for band music, which approaches a collection of tones, and for the irregular barking of dogs. He placed tubes of unequal length to his two ears, thereby upsetting the normal diffraction around the head and interposing a longer path on one side than on the other. Obviously, the distortion produced in this manner is of a type not likely to be met in everyday life and affects different frequencies in widely different fashions. He reports that when listening to "a band of three or four instruments played in the open—the notes will be found to be scattered over a wide range, most being to the side of the short tube, some being in front and some being to the side of the long tube. In listening with such a pair of tubes to two dogs furiously barking

the effect is at first quite alarming—one seems to be in the middle of a pack of dogs, some of which are rushing viciously at one's throat."

An illustration of failure to form any image is found in a phenomenon observed in the use of binaural compensators for determining the direction of submarine sounds. The sound is picked up by two submarine telephone transmitters and led to the ears through independent paths. By adjusting the lengths of the paths the image can be shifted from side to side and for practical purposes the setting of the instrument is made by bringing the image exactly to the middle. A fairly definite sound image is formed, but observers report that part of the sound does not merge into this sound image and move in response to the adjustment, but instead appears as a diffuse background of noise.[6] This may be explained on the assumption that, while the images formed from most of the sound components agree sufficiently well that the observer corrects them to a single position, certain components are so distorted by resonance effects inherent in the apparatus that their images are scattered more or less at random. The lack of agreement among any considerable number of these prevents the formation of a second image and causes the sense of diffusedness.

As the distortion becomes still more extreme we should expect the experimental results to depend more and more upon the observer's power of resolution, for as the distortion is progressively increased a condition must finally be reached where the positions of the images are appreciably different for two components whose frequencies are so nearly alike as to make their recognition as separate tones difficult if not impossible. This condition actually occurred in an experiment of Baley's with a sound consisting of a mixture of sustained tones. Its effect on the listener is interesting from the standpoint of subconscious readjustment of discordant data.

Baley's[7] experiment consisted in applying a number of sustained tones to one ear of a musically trained observer and a number of different tones to the other ear, and testing his ability to assign them to their proper sides. So long as the intervals between the tones were fairly large, the observer never failed to locate them correctly. Considering the entire stimulus as a complex sound we may think of the observer as locating the tones individually and finding them to fall definitely into two groups whose images are located one at each ear.

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[6] This interesting phenomenon was called to our attention by Mr. Richard D. Fay of the Submarine Signalling Corporation, who tells us that it has been noted by a large number of observers.

[7] Stephan Baley: *Zeit. f. Psychol. u. Physiol.*, v. 70, 1914, p. 347.

However, when he used six tones which were separated from each other by a single tone interval, the separate components could not be distinguished and a painful sensation was produced. The observer was apparently faced with the situation that to make the observed intensity ratios and phase differences correspond to a single source would involve extremely large corrections in the observed data. On the other hand, his power of tone resolution was insufficient to separate the components and assign them to different sources. It is not surprising, then, that the difficulty manifested itself by painful sensations. While this illustration is taken from an extreme condition of laboratory experiment and may appear to have little bearing on the everyday location of sounds, it is really significant because of the manner in which it illustrates the importance of psychological factors in all cases in which the sound waves are distorted.

Résumé

In the foregoing discussion an attempt has been made to bring out the main features involved in extending the theory of the binaural location of pure tones to cover, qualitatively at least, the location of complex sounds. It has virtually been assumed that the latter involves three processes: first, the resolution of the sound into its component tones; second, the independent (generally subconscious) location of each separate component; and third, the formation of a conscious judgment of the position of the source based on the locations of the individual images. The greatly increased amount of data available when the sound is complex has quite different effects on the final result according as the different images do or do not coincide. If they do, the accuracy of location and the sense of certainty are increased. If they do not, confusion arises, subconscious corrections are called for, and the final result is likely to depend very considerably on the psychological processes and individual prejudices of the particular observer.

10

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A COLOR-MATCH PHOTOMETER
FOR ILLUMINANTS

BY

HERBERT E. IVES

A THREE-COLOR MIXTURE INSTRUMENT
WHICH PROVIDES A PHOTOMETRIC COMPARISON FIELD
OF VARIABLE COLOR BUT FIXED BRIGHTNESS

A COLOR-MATCH PHOTOMETER FOR ILLUMINANTS

By Herbert E. Ives

Color Difference Photometry by Color-Difference Eliminating Means

The various difficulties encountered in the photometry of lights of different color, due both to uncertainty felt by the individual observer in forming a criterion, and to differences in vision among different individuals, are best overcome by the use of auxiliary standards duplicating the color of the light to be measured. Such auxiliary standards may be light sources of the color of those which it is desired to measure, or they may consist of absorbing media so chosen as to make the transmitted light from the standard and test sources of like appearance. These auxiliary standards of color difference are to be calibrated by some approved method in a standardizing laboratory, and when used yield photometric values which are in agreement with the chosen standard method of color difference photometry.

Color-Mixture Auxiliary Standards

A limitation to the use of colored light sources or absorbing media is that the number required to make possible color matches with all the different colored lights which may be the object of measurement is very large. Some types of colors, such as those of a black body at different temperatures, may all be embodied in a single standard operated under a series of conditions, e.g. voltages, but even so the problem of establishing a series of auxiliary color standards is quite serious, especially in experimental or testing laboratory work where all sorts of illuminants or other colored lights may be the objects of measurement.

The possibility of constructing an instrument on the *color mixture* principle, by which all colors which it is desired to measure may be matched by the simple mixture of a few chosen primaries, has been long recognized. Three-color-mixture measurements of illuminants made by the writer some years ago[1] in fact merely need the ascription of the proper luminous values to the three primaries to make the measurements carried out at the same time measurements of the

243

luminous values of the light sources studied. The first detailed suggestion, however, for a color-match photometer using the mixture principle is due to v. Voss.[2] Voss' proposal was to choose a red, green and blue of equal luminous value and provide means so that as the mixing proportions of the three primaries were changed the sum of the luminous values would remain fixed. In this way the color mixture instrument provides a reference standard or comparison lamp of constant intensity but of any desired color. v. Voss built a two-color instrument according to these ideas, the two colors being so chosen that a series of black body colors corresponding to the majority of the incandescent lamps could be approximately matched. His method of working out his idea, which involved receiving the light from illuminated milk glass surfaces, is probably not at all feasible for a three-color instrument, because of the very small luminous value of the blue primary. He does not appear to have undertaken the actual construction of a three-color instrument.

Objections to a Three-Color Mixture Instrument

In a discussion of the possibility of performing light measurements by the use of a three-color match reference standard some years ago[3] it was pointed out that a very serious practical difficulty is presented by the fact that measurements made by different observers are apt to differ quite widely. The chief reason for this is that the red, green and blue primaries which one ordinarily would decide to use, are quite narrow isolated bands of the spectrum, while the colors which it is desired to measure—for example, those of illuminants—are of quite different spectral character, consisting of continuous spectra of slowly changing intensity from one wave length to another. As a consequence, the relative proportions of the primaries which constitute a match for some illuminant with one observer will not do so for another. This difficulty was considered by the writer at that time as sufficient to discourage any attempt at the practical realization of such a method of color difference elimination at the photometer field.

A second difficulty presented by the three-color mixture idea is one referred to above, namely, that the blue light necessary is of such low luminosity that any means for maintaining the luminous contributions of the three primaries approximately equal, would demand a prohibitively large light source to provide the blue primary.

PRINCIPLES OF THE NEW INSTRUMENT

The fundamental ideas which have made possible the construction of a new instrument in which the difficulties just oulined are very completely overcome, are as follows: It was first of all decided that the instrument would be planned to meet only very moderate requirements as to the range of colors to be measured. It was designed merely to take care of practical illuminants, with no attempt to measure saturated colors. By thus restricting the range of the instrument as to color, it is possible to use primaries very much less saturated than the typical red, green and blue of a universal colorimeter. Such unsaturated primaries when mixed yield lights which extend without gaps over the entire visible spectrum instead of the narrow isolated colored bands of the more ambitious colorimeters. Consequently the differences in the nature of the color under measurement and its copy are minimized.

The possibilities and significance of this limitation of the range of colors to be covered is illustrated by the color triangle in Fig. 1 whose primaries are the fundamental sensations of Koenig, as modified by the writer.[4] In this color triangle are plotted the spectrum, which is shown as a curve marked in wave-lengths, and a series of illuminants ranging from the Hefner lamp to a deep blue sky and including such various light sources as the Welsbach mantle, the carbon arc and the glass and quartz mercury arcs. It will be noted that all the illuminants may be enclosed in a triangle which is much smaller than the fundamental primary triangle and lies far inside the spectrum. This means that all of the illuminants may be matched by mixtures of primaries which are approximately an unsaturated yellow, an unsaturated green and an unsaturated blue. Depending upon how many of the practical illuminants it is desired to bring within the range of measurement, these primaries may range all the way from moderately saturated colors (triangle ade) when all practical illuminants are to be handled, to colors which might be described as little more than tints (triangle acg) where only the lower temperature incandescent solids must be matched. In the instrument which is to be described below the primaries chosen were such that the triangle which they form encloses all the practical illuminants shown in the diagram. With the primaries as chosen the light formed by their mixture is in every case a close approximation to a smooth continuous spectrum, matching very closely in spectral composition all the continuous spectrum illuminants, which

constitute the majority of practical light sources. It is, therefore, to be anticipated that this limitation in the range of colors to be measured will result in overcoming to a very complete degree the objection to three-color mixture instruments due to their common characteristic of providing light of different spectral composition from that of the test color.
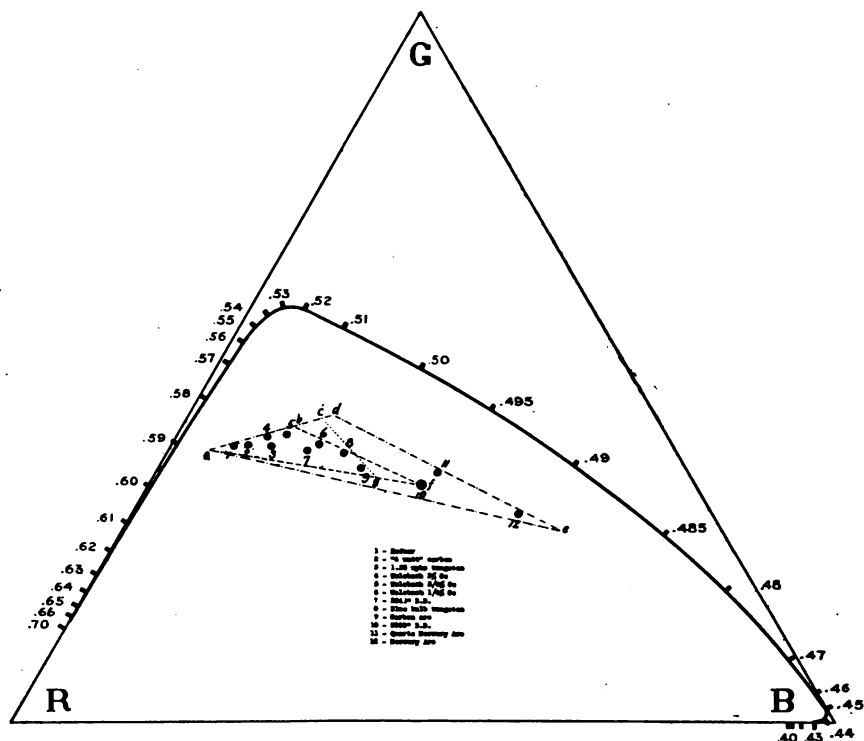

FIG. 1. *Color-triangle, showing positions of practical light sources, and various possible choices of primaries to form mixtures to match some or all the light sources.*

The second factor contributing to the practical success of the new instrument is the choice of the optical system. The central feature of this is a condensing lens whose aperture is covered with the absorbing media which serve to produce the three colors used as primaries. The image of a light source formed by the condensing lens is focused on the translucent side of a small diffusing chamber, an inner wall of which is observed. By this means a very efficient utilization of the light available from the comparison standard is attained, so that even the blue primary can be obtained of an intensity of practical value.

CONSTRUCTION

The construction of the color-match photometer is shown diagrammatically in Fig. 2 in plan and elevation.   S is the illuminant used as source for the light of the three primary colors.   It consists of a 400 watt Type "C" Mazda lamp, with the filaments lying all in one plane within a rectangle of a 1½ c.m.² This is a lamp commercially manufactured for moving picture projection. L_1, L_2 are two plano-convex
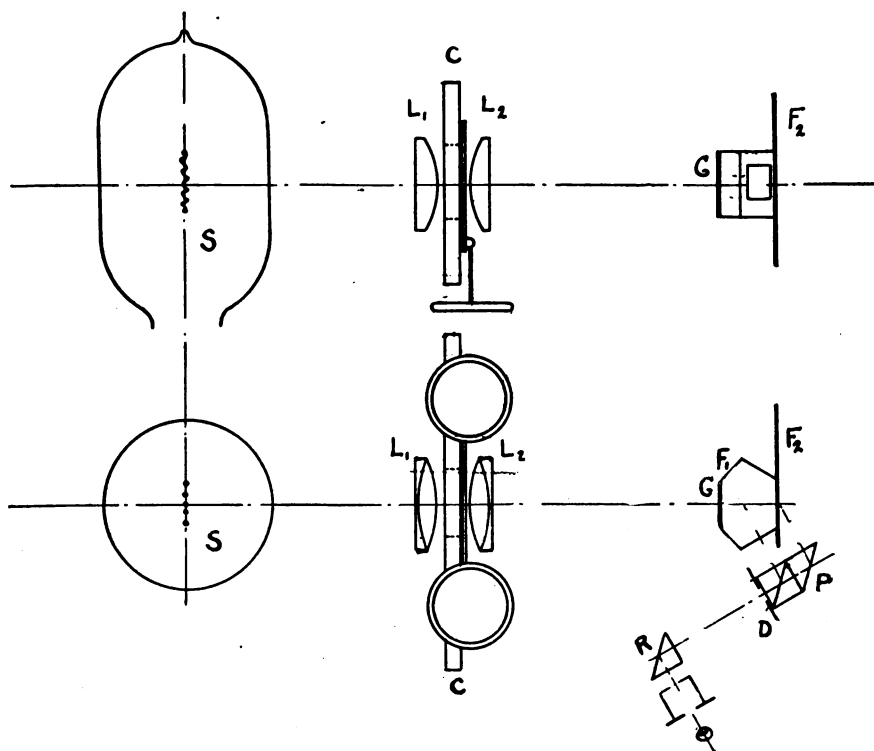

FIG. 2.   *Plan and elevation of color-match photometer.*

achromatic lenses of 20 centimeters focal length each.   At C stands the frame holding the colored glasses and the variable apertures shown on an enlarged scale in Fig. 4, which will be described in the next paragraph. At F_1 stands a small hexagonal box with walls white on the inside, and provided with a ground glass window at G.   The image of S is focused upon the ground glass and the light falling upon the side F_1 reaches it, partly by diffusion from this glass and partly by reflection from the other walls. F_2 is an extended white surface intended to receive the light from the source under measurement. F_1 and F_2 are observed in

juxtaposition by means of a photometric prism P. A right angle prism R is interposed in the line of sight in order to make the observing position one of maximum convenience. A diaphragm D restricts the field to 3° diameter. The photometric field used is of the contrast form, and is illustrated in detail in Fig. 3. Light from F_2 is totally
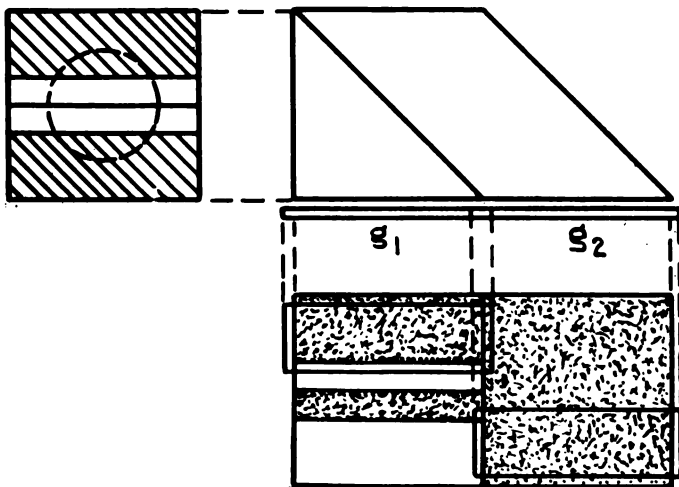

FIG. 3. *Detail of photometric prism and contrast field.*

reflected by the silvered hypothenuse of the prism most distant from the eye; while the hypothenuse of the nearest prism is silvered in horizontal strips from which the light from F_1 reaches the eye. Four strips are visible in the field, and the two outer ones are reduced in brightness by the interposition of clear glasses g_1 and g_2 as shown in the figure.
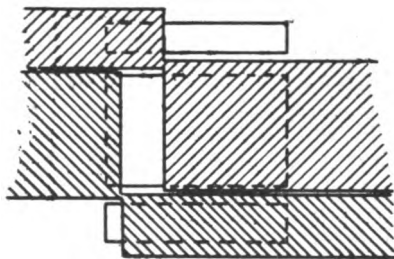

FIG. 4. *Arrangement of sliding diaframs to insure constant total length of filter openings.*

In Fig. 4 is shown diagrammatically the arrangement of the colored glasses and variable apertures which are used to control the composition

of the light falling upon the diffusion chamber. The colored glasses consist of a yellow, green and blue whose spectral transmissions will be described in a following section. These glasses are covered by fixed apertures of such width that the luminous intensities of the lights transmitted through equal lengths of the apertures are equal. Directly over the fixed apertures are the variable apertures, which are formed of two flat sheets of metal cut in a "zig-zag" pattern so that each sheet lies partly over each of two of the fixed apertures in such a manner as to cover exactly that fraction of the length of one which it uncovers of the other. It will be clear then, from inspection of the figure, that as the two thin sheet figures are moved back and forth varying ratios of the three primaries are exposed but that the sum of the lengths of the fixed apertures is always constant; in other words, that the luminous intensity of the light projected on the diffusion chamber is constant while the color may be varied to any value within the range of the mixtures possible with the three primaries used. This arrangement is essentially that described by v. Voss.

The frame holding the colored glasses and special variable aperture diagram is shown in the photograph, Fig. 5, and the complete photometer as built is exhibited in the photograph Fig. 6.

SELECTION OF PRIMARIES

The yellow, green and blue primaries which were embodied in the instrument as constructed, were chosen from commercially obtainable colored glasses which presented desirable qualities as to the nature of their spectral transmission and the uniformity with which they could be produced. They are all from the list of the Corning Glass Company. The yellow bears the maker's number G-30-B and is called "high transmission yellow." The green is a combination of G-40, called "admiralty green" and a yellow green, called G-408-N. The blue is entitled "daylight," G-90-A. Samples of these glasses, which from preliminary inspection of their spectral transmission curves appeared likely to be of approximately the correct color, were measured on the spectro-photometer and transmission curves worked out for varying thicknesses.

In order that these glasses in any chosen thickness should make available definite colors, it is of course necessary that the radiant used should be of definite and known character. The radiant selected for this purpose was the black body at 2848 degrees absolute. This choice was made for the practical reasons, first that a color temperature

standard of this value could be obtained from the Bureau of Standards, and second that this color represented a feasible value for operating the
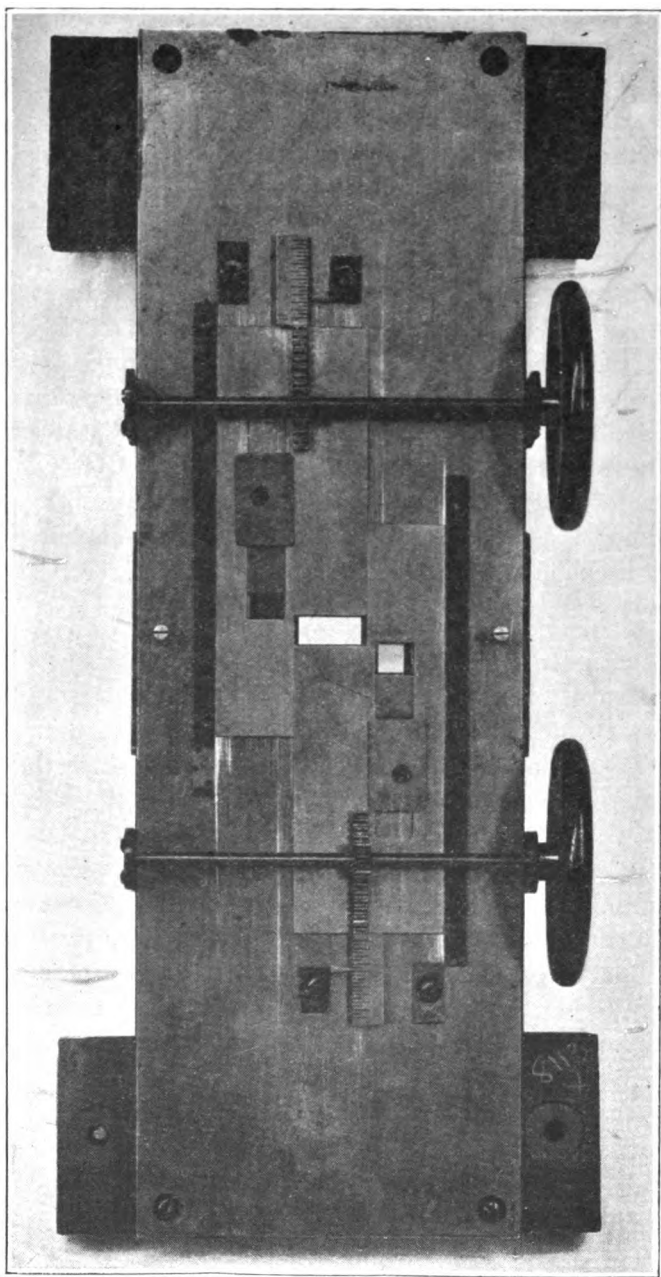

FIG. 5. *Color filter and variable diafram frame.*

tungsten lamp which was selected for the light source embodied in the instrument.
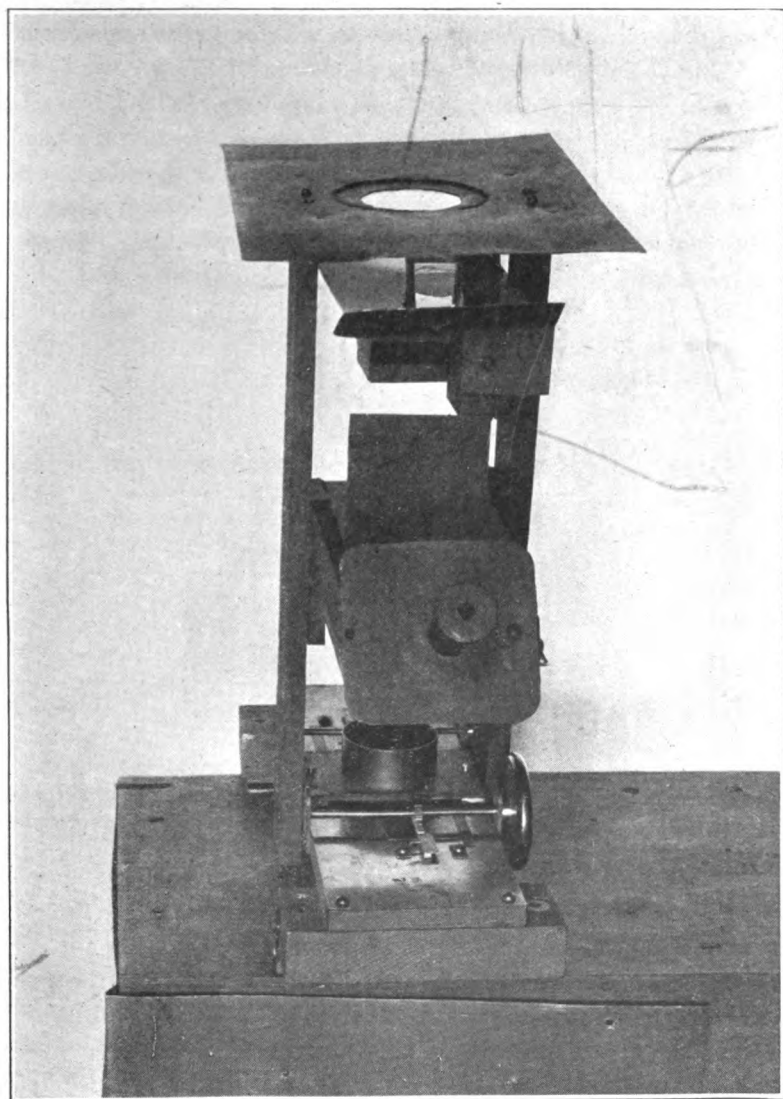

FIG. 6. *Color-match photometer.*

Taking the transmission curves for the three glasses and multiplying the black body energy distribution at each wavelength by these transmission values a set of energy curves was obtained corresponding to various thicknesses of these glasses. These energy curves were multi-

plied at each wave-length by the color sensation curves of the equal
energy spectrum.   The resultant sensation values for the various
colors so obtained were then plotted in the same color triangle as that
in which the values of the illuminants were already approximately
known.   Fig. 7 shows diagrammatically how the colors corresponding
to various thicknesses of these glasses in combination with a black body
at 2848 degrees move out on the triangle from the point corresponding
to the 2848 degrees black body.   From this diagram it was then
possible to select thicknesses which would give colors suitable for
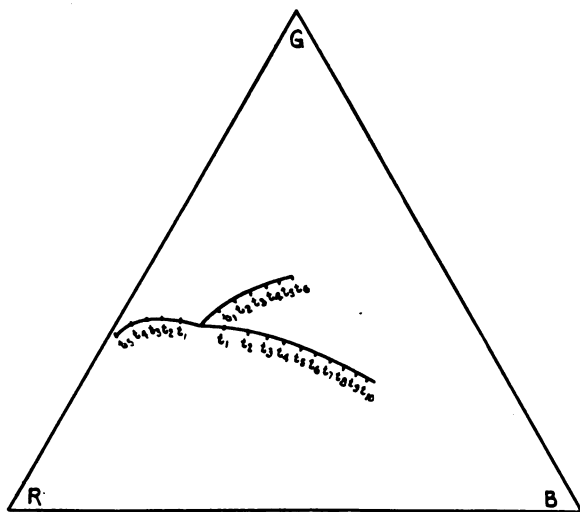primaries whose mixtures would match all of the practical illuminants.

FIG. 7.   *Colors obtained by using various thicknesses (t) of special colored glasses
over 2848 degree black body.*

The next step consisted in determining the luminous values of the
lights received through these glasses.   These values might have been
determined by photometry of the integral light, by the photometric
procedure which has been advocated by the writer.   In the present
case, however, it appeared simpler to arrive at the same results through
the use of the spectral luminous efficiency curve which was obtained
through the same photometric procedure and has been checked with
that procedure through the physical photometer.[5]   Accordingly, the
spectral energy distribution curves for the three colored lights were
multiplied wave-length by wave-length by the luminous efficiency
curve of the spectrum.   The areas of the resulting curves give at once
the relative luminous values of the three illuminants when equal

areas are used of the three glasses. From these relative values it is a straightforward matter to calculate the relative areas of the three glasses which should be chosen in order that the light transmitted should be of equal luminous value from each. .These figures give the widths of the fixed apertures.

These fixed apertures were made in the following manner: A large template was cut in white Bristol board. This was then photographed down to the required size on photographic plates especially flowed with the emulsion on plate glass. Contact prints from the negatives so obtained were made on similar plate glass plates coated with a special contrast emulsion. These contact prints when developed to high density and cleared with reducing solution provided accurate templates of the required size, as shown in Fig. 8. The three colored

FIG. 8.   *Template for color filters; top, yellow; middle, blue; bottom, green.*

glasses, built up into blocks of uniform thickness by the addition of plates of clear glass, were cemented to this template embodying the three fixed apertures of the calculated ratios.

An important condition which must be met by the color match photometer is that the brightness of the photometer field must be not only adequate to obtain photometric precision but that it should correspond accurately to the brightness at which the method of color difference photometry which is chosen is required to be carried out. This latter requirement is indeed of relatively little importance where the light on the two sides of the photometric field is very closely the same in spectral composition, as it was the intention should be the condition here. At the same time such light sources as the mercury arc do differ so much in composition from the mixed light with which they are compared that the adherence to standard field brightness conditions is highly desirable. In the present case the field brightness

which is to be attained is that of a white surface under twenty-five meter candles illumination. In order to obtain this it is necessary to properly proportion the size of the light source, the focal length of the lenses and the size of the lens aperture. The apparatus as worked out with the 400 watt lamp as described, gives very accurately this brightness; it appears quite possible, however, to shorten up the instrument so that a 100 watt lamp would suffice.

It is of interest to note the degree to which the conditions laid down in planning the instrument have been met. Fig. 9 shows at Y, G, and B the positions in the Koenig fundamental sensation triangle of three primaries chosen as computed from their energy distributions, and also the twelve artificial illuminants already shown in Fig. 1. All of these are included within the color-match photometer triangle, the mercury arc and two of the Welsbach mantles being practically coincident with the sides.

The energy distributions of the three primaries as used are shown in Fig. 10. It will be noted that they correspond to rather extended, fairly uniform, continuous spectra. The most instructive representation of their performance is given by plotting the spectral distribution of energy as incident upon the diffusion chamber when typical light sources are matched in color. In Fig. 11 is shown the energy distribution due to the mixture which gives a visual match with the 5000 degree black body, as obtained from a combination of tungsten lamp and daylight glass[6] which was in turn matched against the synthetic color apparatus described in a previous paper.[7] It will be seen that the energy distribution of the mixture plots as a fairly smooth curve weaving up and down around the 5000 degree black body distribution. It is in fact quite as close an approximation as is attained by any of the successful artificial daylight units now in commercial use.

Fig. 12 shows similar data for the black body at 2848 degrees K. It is obvious that where the light sources under measurement present a continuous spectrum, the color-match photometer presents a mixture which not only matches the integral color of the illuminant but is a very close match for energy distribution. Trials with several observers show that all set alike on illuminants of this class.

The case is, of course, different where light sources such as the mercury arc are measured, for here the color-match photometer gives a continuous spectrum while the light source has a line spectrum. It is obvious that with such differences in spectral composition different readings are to be expected by observers of different color vision
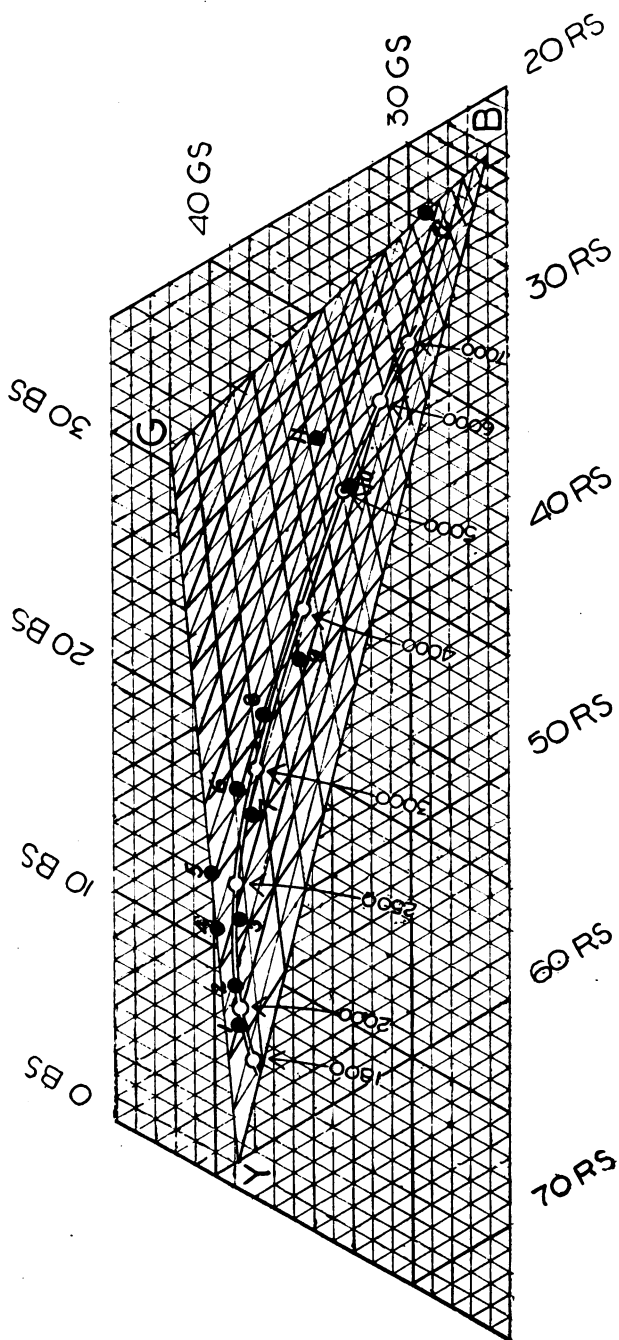
FIG. 9. Color triangle of color-match photometer superposed on sensation triangle; 1-12, illuminants as listed in Figure 1.

characteristics. It has, however, been considered much better to sacri-
fice the accuracy of the instrument in the case of the rather unusual
light sources in favor of the unusual continuous spectrum sources. It
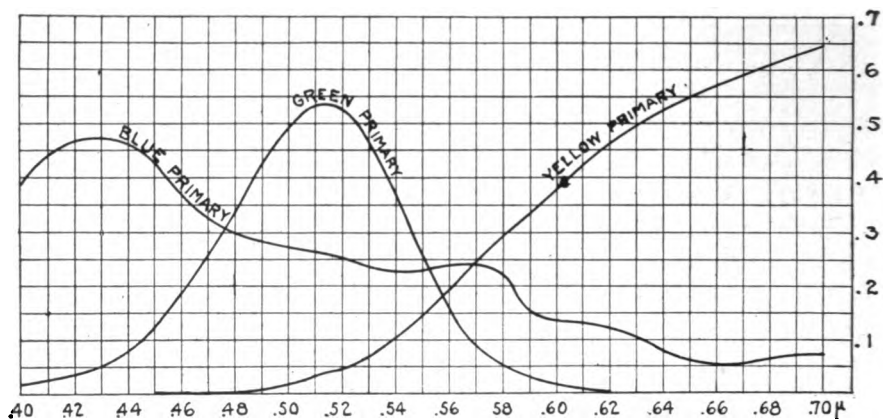will be noted that the unsatisfactory character of the energy distribu-

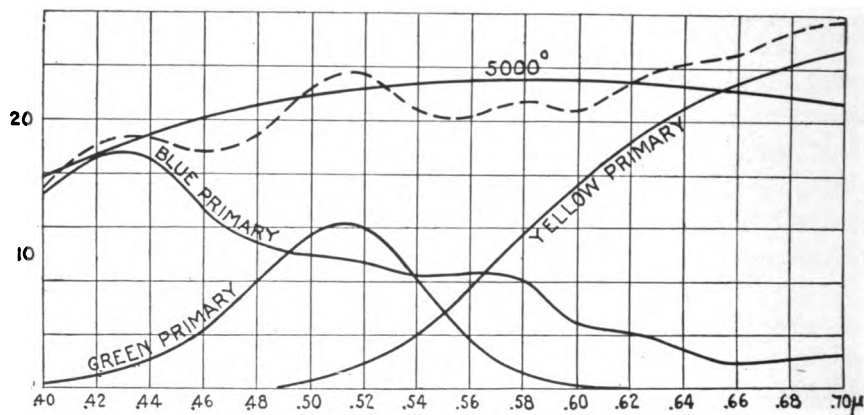FIG. 10. *Spectral energy distribution curves of primaries.*

FIG. 11. *Energy distribution of color-match photometer setting for 5000 degree
black body color, compared with true distribution.*

tion match in the one practical case of the mercury arc corresponds
to the universally unsatisfactory character of the matches made by a
color mixture instrument using pure red, green and blue as its prima-
ries.

Use of the Instrument as a Photometer

The use of this instrument as a color-match photometer is extremely simple. Let us suppose that our photometric standard is a carbon incandescent lamp. We imagine the color-match photometer as placed upon the photometer bench in a fixed position and that the carbon lamp is movable. We first set the comparison lamp S (Fig. 2) at that voltage at which it accurately color-matches a black body at 2848 degrees. This may be done by swinging the colored glasses to one side and matching the lamp against a color temperature standard
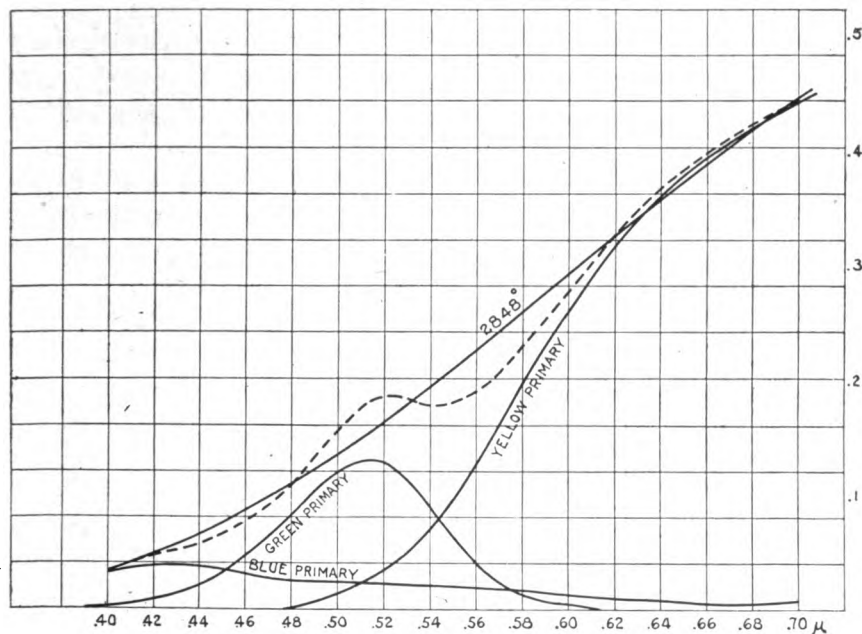

Fig. 12. *Energy distribution of color-match photometer setting for 2848 degree black body color, compared with true distribution.*

or against the standard "four watt" carbon lamp by introducing some standard absorbing medium which exactly annuls the color difference between the four watt lamp and the high efficiency comparison lamp. For this purpose the Fabry yellow absorbing solution, described in an earlier paper,[8] in a concentration of 30%, is admirably suited. With the colored glasses back in place the ratio of the three colors is altered by trial, by turning the large heads to the pinions projecting from the color filter frame, until an approximate match is obtained. The carbon lamp is moved until an intensity match obtains and the

color-match is made exact. Photometric settings are then made by moving the carbon lamp in the regular manner. If now it is desired to measure a lamp of some other color—for instance, a high efficiency tungsten lamp—it is substituted for the standard carbon lamp and the ratios of the colors altered by trial until a new color match is obtained. The new lamp is then moved back and forth until a match both for color and intensity is obtained. The ratios of the intensities of the tungsten lamp and the carbon lamp are then obtained by the inverse square law from the positions occupied by the two lamps respectively at their positions of photometric match. Other means of varying the illumination of the surface F_2, such as a variable sector disc or variable transmission gratings, may, of course, be used. The characteristic feature of this apparatus is that it provides a comparison "lamp" of fixed intensity but of any desired color.

The measurements obtained are then on that photometric scale which is embodied in the luminous efficiency curve of the spectrum which is used in calculating the luminous intensities of the radiations received from the three color filters. The curve which has been used in the construction of this photometer is that derived by the author, which has been intercompared in various ways with other measurements made in accordance with the photometric conditions, and the average eye recommended by the writer.[5]

USE OF THE INSTRUMENT AS A COLORIMETER

By means of divided scales attached to the metal slides which govern the openings of the color filters, it is possible to obtain the relative amounts of yellow, green and (by subtraction from unity) blue, needed to match the color of the illuminant under measurement. These quantities constitute a measurement of the color of the illuminant in that trichromatic system whose primaries are the yellow, green and blue defined by the spectral energy distribution curves shown in Fig. 10. These yellow, green and blue values can be plotted—for instance in a color triangle,—and constitute a complete record of the color measured.

It is, however, undesirable to record trichromatic measurements in terms of such very special primaries as those here used. The preference both in this case and in other cases of the use of trichromatic measuring instruments is to reduce the readings to some fundamental scale of reference, for instance, the fundamental color sensation triangle as established by the researches of Koenig. In previous papers[4] the

procedure necessary to reduce the trichromatic measurements made with any set of primaries, to their equivalent values in terms of another set, has been developed. This process has been applied in Fig. 9 to the primaries of this instrument. The large external triangle (shown only in part) has for its vertices the fundamental sensations as represented by the Koenig curves as modified by the present writer. The small interior triangle has for its vertices the primaries of the instrument here under discussion. The divisions of the small triangle, which vary greatly in absolute magnitude from one vertex to another, are equal divisions of the color-match photometer scales. In order, therefore, to reduce the color-match photometer readings to fundamental sensations, it is only necessary to find the location of the point whose coördinates are given in terms of yellow, green and blue in the small triangle and then read off this position on the larger underlying figure. On this same triangle have been plotted calculated colors of various black bodies, taking the black body at 5000 degree absolute as the white center for the color sensation triangle.

In the papers on the transformation of color measurements from one system to another already referred to,[4] graphic means are described for transforming trichromatic measurements to measurements in terms of spectrum hue, saturation and luminosity. By utilizing the rules of that paper it is possible to transform the yellow, green and blue measurements made by the color-match photometer to luminosity, hue and saturation values. The diagram to be used for this is shown in Fig. 13. Here the color-match photometer triangle is drawn superposed on the monochromatic diagram. The divisions on the triangle are marked merely along the sides in order to avoid too great confusion of lines. The method of using this diagram is as follows: A color having been measured by the color-match photometer in terms of yellow, green and blue mixing proportion, the point corresponding to this is found by the use of a straight edge laid between the appropriate coördinates along the triangle sides. This point established, a line is drawn from the white center of the sensation triangle through the point until it cuts the spectrum. From its point of intersection, the spectrum hue is read off. The saturation or percentage in luminosity units of the spectral color is read from the "contour lines." The luminosity of the measured light is obtained, of course, by the use of the instrument as a photometer in the manner already described.

It is necessary to emphasize the fact that these transformations while fully worked out as to method can not be expected to check

completely with direct measurements carried out with other trichromatic primaries or by monochromatic analyses, due to the meagre data from which the diagrams 9 and 13 are constructed. In so far as color measurement in fundamental units is in question, therefore, these diagrams represent an ideal as yet only approximated to, as will be
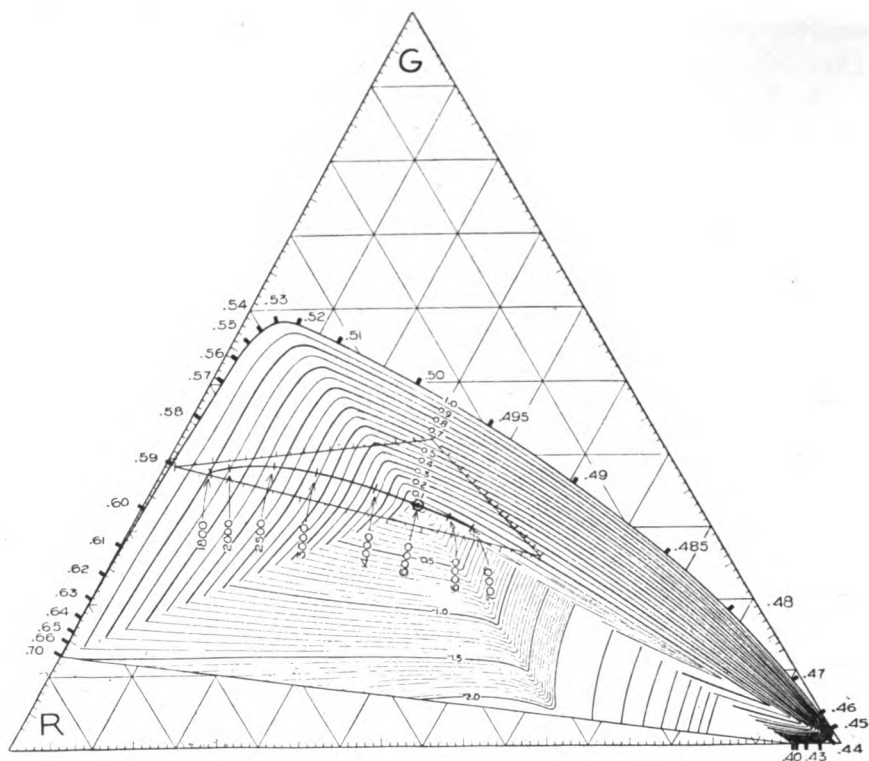

FIG. 13. *Diagram for transforming color-match photometer measurements to*
(1) *Sensations,*
(2) *Spectrum hue and saturation,*
(3) *Black body temperature color.*

shown in a subsequent paper. No such limitation exists, however, on the use of the instrument as a photometer. It offers an eminently practical solution of the problem of color difference photometry in the case of illuminants.

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THE CRYSTAL STRUCTURES OF THE SYSTEM PALLADIUM - HYDROGEN

BY

L. W. McKEEHAN

A STUDY
BY MEANS OF X-RAY CRYSTALLOMETRY
OF THE OCCLUSION OF HYDROGEN

THE CRYSTAL STRUCTURES OF THE SYSTEM PALLADIUM–HYDROGEN.

BY L. W. McKEEHAN.

ABSTRACT.

Crystal structures of the system palladium-hydrogen.—Palladium in the form of a fine wire, 1/4 mm diam., or of a narrow strip 1/20 mm thick, was more or less saturated with hydrogen and used to diffract x-rays of known wave-length as in the well-known powder method. Two crystal structures were present, both having a face-centered cubic arrangement of atoms. One, that of pure palladium, has a parameter 3.900×10^{-8} cm, while the other, that of hydrogen-saturated palladium, has a parameter varying between 4.000 and 4.039×10^{-8} cm, depending on the degree of saturation. A value near the upper limit, say 4.036×10^{-8} cm, probably corresponds to a *compound* Pd_2H, with a *density* of 10.76 gm/cm³. The arrangement of atoms may be as in Cu_2O, but there is no x-ray evidence for the positions of the hydrogen atoms. *Stability*. All the evidence so far obtained indicates that in the absence of sufficient free atomic hydrogen, the saturated state is unstable or metastable and that return to the hydrogen-free condition once initiated in any crystal proceeds rapidly to the end; also pure palladium is unstable in the presence of atomic hydrogen.

Occlusion of hydrogen by palladium.—A *necessary condition* is the presence of atomic hydrogen which may be supplied by electrolysis or by surface dissociation of hydrogen at high temperatures. The *penetration* into the wire was shown to be relatively slow; in the case of the strip it was somewhat irregular, probably depending on the orientation of the crystals. The crystal evidence provides an *explanation of the variations of electric resistance*. A *bibliography* of 66 titles, mostly 1900–1921, is appended.

THE effect of occluded hydrogen in increasing the electrical resistance of palladium has long been known to be, over a considerable range, a linear function of the amount of hydrogen taken up,[1] and in a study of the factors affecting electrical resistance it seemed of interest to find out, if possible, in what way the hydrogen entered and was held during the process. A direct and available method of attack was that of measuring the changes in crystal structure produced by the process of occlusion. The crystal structure of palladium was first determined by Hull[2] to be based on a face-centered cubic space-lattice. Metal of exceptional purity, samples of which had been analyzed by the same method in this laboratory,[3] was available for the present research.

[1] W. E. McElfresh, Am. Acad., Proc., *39*, 323–335 (1904).
[2] A. W. Hull, PHYS. REV. (2), *17*, 571–588 (1917).
[3] L. W. McKeehan, PHYS. REV. (2), *19*, 537–538; *20*, 424–432 (1922).

There appeared to be some confusion in the considerable literature of palladium-hydrogen systems,[1] as to the possible methods for obtaining high concentrations of hydrogen within the metal. The methods found effective in the present series of experiments furnish support to the theory of the process here advocated, and will therefore be discussed in connection therewith after description of the observed crystal structures.

The powder method of x-ray crystallometry has been described so often that it will suffice to state here that the K-radiation of molybdenum, filtered through zirconium oxide,[2] was used, in which the two photographically important wave-lengths are 0.71212×10^{-8} cm and 0.70783×10^{-8} cm. The mean radius of the cylinder of photographic film was 20.36 cm. The palladium was either a wire 0.025 cm in diameter or a strip[3] about 0.3 cm wide by 0.005 cm thick. The exposures used were of the order of 500 milliampere-hours. In no case were the grains, even after prolonged annealing, large enough to give separately distinguishable diffraction spots,[4] so that measurements were always made to the edges of smooth bands on the negative. Twenty or more such bands of the principal pattern present were almost always of sufficient intensity to permit their use in calculations, and the mean values of the parameters for the face-centered cubic space-lattices always observed are believed to be correct for each film to within one part in three hundred. Seventeen photographs were taken under various conditions.

There is a fairly well-defined limit in concentration of hydrogen below which the hydrogen is taken up with much greater facility, and the state reached at this limit may therefore with propriety be called the saturated state. If excess hydrogen be taken up the state can be described as supersaturated. With one exception, noted below, supersaturated states were probably not obtained. The method of examination, requiring as it does a relatively long time, is not well adapted to the study of conditions probably as transient as that of supersaturation at ordinary temperatures. Since the change in resistance follows a non-linear law above saturation, it was felt, also, that the lower range of concentration was of chief interest.

In the first experiment a thin strip of metal was, after preliminary annealing, examined first in air and then in a stream of commercial hydrogen, at atmospheric pressure. By what must now be regarded as a happy accident, the strip took up enough hydrogen to saturate it. The parameter of the face-centered cubic lattice of hydrogen-free pal-

[1] See appended bibliography.

[2] W. P. Davey, Optical Soc. America, J., *5*, 479–493 (1921).

[3] L. W. McKeehan, Frank. Inst., J., *193*, 231–242 (1922).

[4] L. W. McKeehan, Frank. Inst., J., *194*, 87–92 (1922).

ladium is [1] 3.900. The pattern here obtained with hydrogen-saturated metal was similar to that of pure palladium, the parameter however being 4.038, or 3.5 per cent greater. This preliminary result has already been reported.[2]

In later experiments with the same strip it was found that after expulsion of the hydrogen by heating, the crystal structure became that of pure palladium again, but an attempt to repeat the cycle failed. This was traced to sulphidation of the surface, the hydrogen used being not quite free from H_2S. Other strips showed very little occlusion of carefully purified gaseous hydrogen at room temperature, whether treated immediately after rolling down or after annealing for a few hours at around 800° C. The electrolytic process, however, in which the palladium is made the anode in a weak solution of sulphuric acid, never failed to introduce any desired amount of hydrogen up to saturation. Another process [3] found efficacious was to heat the palladium in a vacuum furnace to about 1100° C for an hour or more, turn off the heating current, and admit gaseous hydrogen when the temperature of the furnace had dropped to about 700° C. This had the disadvantage, however, as compared with the electrolytic method, of not permitting partial saturation. The anomalous result of the first test is now ascribed to the hydrogen sulphide present in the gas which furnished enough atomic hydrogen at the surface during the formation of palladium sulphide to saturate the thin layer of metal underneath.[4] Subsequent attempts failed because of the protecting coating formed by this process.

Wires and strips partially saturated by the electrolytic method gave diffraction patterns in which each line was doubled. The clear space between the lines of each pair shows that crystals of two definite sorts are present, there being few if any crystals with intermediate dimensions. The ratio of intensities varied widely depending upon conditions. In the case of wires about 0.025 cm in diameter, no unsaturated metal lay near enough to the surface to contribute to the photograph if the increase in total resistance amounted to more than 30 per cent, the increase at saturation being nearly 70 per cent. When the saturated surface of partially saturated wires was removed by aqua regia the diffraction pattern due to unaffected metal was relatively intensified, confirming the conclusion that the penetration of hydrogen into the metal is progressive. With partially saturated strips 0.005 cm

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[1] In Ångstrom units; to reduce to centimeters multiply by 10^{-8}.

[2] L. W. McKeehan, PHYS. REV. (2), *20*, 82 (1922).

[3] R. M. Holmes, Science, *56*, 201–202 (1922).

[4] Cf. E. B. Maxted, Chem. Soc., J., *115*, 1050–1055 (1919); *117*, 1280–1288 (1920); *119*, 1280–1284 (1921).

thick the distribution of saturated crystals over the surface of the strip was irregular, as shown by imperfection in the resulting patterns. It is probable that differently oriented crystals become saturated with different facilities.

The smaller parameter obtained from the double patterns showed about the degree of variation usual in crystallometry of a pure metal [1] and was apparently to be ascribed to pure palladium, the range of values being from 3.889 to 3.906. The larger parameter showed a greater variability, ranging from 4.000 to 4.039, which corresponds to a range of 0.24 cm in the position of the line due to reflection from the (531) planes of the lattice, the last lines visible in faint patterns. This range is considerably more than the probable error in measurement. The intensity of reflection was never considerable, however, unless these crystals had parameters in excess of 4.010, and the values for the parameter obtained from intense photographs cluster in the range between 4.023 and 4.039, indicating the existence of a true limiting value somewhere in this range; the value 4.036 is preferred.

An attempt was made to reduce the parameter of saturated crystals by heating them for a short time at 200° C, which treatment reduced the excess resistance in a particular case from 75 per cent, corresponding to slight supersaturation, to 30 per cent. Before heating, the single parameter apparently present was 4.038; after heating the two values 4.025 and 3.900 were obtained, the intensities being roughly the same for the two patterns. Judging by the greater breadth of the lines in the second experiment as compared with those usually observed, the crystals of both sorts were either very small or were badly strained.

An attempt has been made to find places for the hydrogen atoms in the saturated crystals which would at the same time satisfy the observed cubic symmetry and the formula Pd_2H proposed by earlier investigators for a supposed hydride. The process of occlusion would on this basis be analogous to the volume oxidation of calcium crystals, where the introduction of the oxygen atoms actually pulls the metal atoms closer together,[2] and where the process stops definitely at the composition CaO. The low atomic weight of hydrogen makes any such hypothesis regarding its arrangement purely speculative since the proposed structure cannot be checked by intensity measurements. The arrangement already familiar in Cu_2O and Ag_2O is suitable, and, nothing being known about the crystallographic properties of the hypothetical Pd_2H except the facts here recorded, cannot be contradicted. This would place the hydrogen atoms on a body-centered cubic lattice with the same parameter as that

[1] L. W. McKeehan, PHYS. REV. (2), *19*, 537–538; *20*, 424–432 (1922).

[2] A. W. Hull, PHYS. REV. (2), *17*, 42–44 (1921).

here found for the face-centered cubic lattice of palladium atoms, the points of the former lying symmetrically on the trigonal axes (cube body-diagonals) of the latter. This is expressed more formally by stating that palladium atoms occupy the points $(0, 0, 0)$, $(0, a/2, a/2)$, $(a/2, 0, a/2)$, $(a/2, a/2, 0)$ and hydrogen atoms the points $(a/4, a/4, a/4)$, $(3a/4, 3a/4, 3a/4)$, where $a = 4.036$ is the parameter of a simple cubic lattice. The density of the compound Pd_2H would then be 10.76 gm/cm^3, that of Pd being [1] 11.87 gm/cm^3. Another possibility is to put both of the two hydrogen atoms absorbed by each face-centered cube of palladium atoms at the centers of opposite faces of one of the eight smaller cubes into which it can be divided. This preserves the identity of the hydrogen molecule as the other arrangement does not, but is less symmetrical, requiring a unit of structure containing 108 palladium atoms and 54 hydrogen atoms to attain cubic symmetry, and is therefore improbable. The variability in the parameter of saturated crystals is against the idea of a definite compound being formed in every case. It is probably only the limit which is approached more or less closely, depending upon the temperature and other factors determining the equilibrium condition.

CONCLUSION.

The phenomena here observed seem consistent with the following physical assumptions, some of which have been previously made by others:[2]

1. Palladium and hydrogen are not miscible in all proportions at ordinary temperatures and pressures. Two crystalline phases can coexist, one being practically pure palladium, the other a saturated solution of hydrogen in palladium.

2. The amount of hydrogen in a saturated crystal of palladium, and the distention of the crystal space-lattice thereby, decrease with increase in temperature and with reduction in pressure of dissociated hydrogen in the neighboring space.

3. Unsaturated crystals in conditions favorable to saturation become saturated very rapidly because the introduction of any hydrogen atoms into the interatomic spaces so strains the space-lattice that the entrance of additional hydrogen atoms is facilitated.

4. Saturated crystals are in unstable or metastable equilibrium in air and lose hydrogen by diffusion at a rate which is accelerated by heating. Desaturation once started in any crystal proceeds rapidly to the end because of the intense local strains set up by the removal of a few hydrogen atoms.

[1] L. W. McKeehan, PHYS. REV. (2), *19*, 537–538; 20, 424–432 (1922).
[2] See appended bibliography.

5. An unsaturated crystal lying too deeply below a surface exposed to atomic hydrogen at ordinary temperatures is unaffected until a considerable part of its bounding surface is covered by saturated crystals, because hydrogen can reach it through neighboring crystals or through intercrystalline amorphous metal by slow diffusion only, and it therefore becomes exposed to hydrogen in quantity only by the opening of pores by expansion of the overlying crystals.

6. The linear resistance-change throughout the greater part of the range of occlusion is due to the varying proportions of the two sorts of crystals which, in consequence of (3) and (4), are the principal constituents of the system.   This type of resistance-change is, in fact, a criterion for alloys which are mechanical mixtures of two phases.

7. The small initial rise in resistance and the final slow approach to a limiting value are due to changes in the resistance of intercrystalline material or to defects in intercrystalline contact, or to both.

8. The temporary change in resistance observed when the process of saturation is interrupted [1] is due to the transient presence of partially saturated crystals, the whole mixture simulating the condition of a uniformly dispersed solid solution.

9. Occlusion requires the presence of atomic hydrogen, which may be supplied either by electrolysis at ordinary temperatures or by surface dissociation of gaseous hydrogen at high temperatures.

The appended bibliography may be of service in coördinating the experimental studies in this field in the light of the new crystallographic data.

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RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY, AND THE WESTERN ELECTRIC COMPANY, INCORPORATED.
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THE CRYSTAL STRUCTURES OF SILVER-PALLADIUM, SILVER-GOLD, AND IRON-NICKEL ALLOYS

BY

L. W. McKEEHAN

Two Papers Dealing with
Variations of Crystal Parameter with Composition
and Probable Causes of Minor Variations from
Linear Changes

THE CRYSTAL STRUCTURE OF SILVER–PALLADIUM AND SILVER–GOLD ALLOYS.

By L. W. McKeehan.

Synopsis.

Crystal Structure of Silver, Gold and Palladium and of Ag-Au and Ag-Pd Alloys.
—Thin ribbons of the pure metals and of seven binary alloys of each series were prepared by fusing into small ingots and then swaging, drawing and rolling to thicknesses of from 1/400 to 1/200 cm. The x-ray diffraction patterns were photographed by allowing the K-radiation of Mo to fall for 8 to 20 hours on each ribbon. It was found that all these metals and alloys have their atoms arranged in face-centered cubic lattices. The parameter a of each lattice, the edge of the cube, has the values 4.08×10^{-8}, 4.075×10^{-8} and 3.90×10^{-8} cm. for pure Ag, Au and Pd respectively. For the Ag-Pd series, the parameter is nearly a linear function of the atomic per cent. of either component and this is also true for the Ag-Au series except that for the alloys with 30, 40 and 60 per cent. Ag the values of a came out one per cent. too high. These results are for the most homogeneous and isotropic condition and are believed to be correct to within about 1/3 per cent. *The effect of annealing* at from 830 to 940° C. for an hour or more in vacuo was to increase the size of individual crystals, to render them more homogeneous and to make their orientations more isotropic. *The effect of moderate cold working*, rolling, pressing or hammering is to reduce the size of the individual crystals and to make them less isotropic.

Densities of crystals of silver, gold and palladium, computed from the above results of X-ray crystal analysis and the atomic weights, come out 10.49, 19.24 and 11.87 respectively. The Ag and Au were pure and the Pd contained only 0.5 per cent. impurity.

Introduction.

A STUDY of the arrangement of atoms in alloys which are solid solutions of the components may throw some light on the cause of the abnormally high resistivity of such alloys. This report covers somewhat completely the crystal structure in two series of alloys, those of silver with gold and palladium, which are particularly interesting in this connection because silver and gold both possess high conductivity, whereas the conductivity of palladium is much lower than that of silver. The conductivity of the alloys is not, however, treated in this report.

Preparation of Alloys.

The component metals were all purchased from Baker and Company, and were of high purity, the silver and gold containing less than 0.01 per cent. of impurities, the palladium containing about 2 per cent. of impurities, chiefly copper and noble metals. The chemical and metallurgical processes outlined below were conducted by Mr. J. E. Harris

and Mr. H. T. Reeve, both of this laboratory, who have had extensive experience in the preparation of alloys of known composition and exceptional homogeneity. All three metals were repurified chemically and obtained in finely divided form, the principal effect of these processes upon their purity being that the palladium finally contained less than 0.5 per cent. of impurities, copper, in particular, being completely removed. The metal powders were weighed, mixed, and pressed into small cylindrical rods of the desired compositions. The Ag-Au alloys were fused in an electrically heated furnace open to the air; the Ag-Pd alloys were fused on alundum or magnesia by the oxyhydrogen flame. The ingots, which weighed about 10 grams each, were swaged and drawn into wires about one millimeter in diameter. Short pieces of these wires were rolled to a thickness of from 0.0025 to 0.0050 cm., the rolling being carried farthest for alloys containing large proportions of gold, and hence having the highest absorption coefficients for x-rays. The condition resulting from these operations is indicated below by the letter R.

The annealing process consisted in maintaining the temperature of the sample at from 830° C. to 940° C. for an hour or more, in vacuo, in a quartz tube furnace, electrically heated. When several alloys were annealed at one time the samples were placed in individual quartz tubes, open at one end, to prevent mutual contamination. Temperatures were read by a calibrated platinum-platinum-rhodium thermocouple. The Ag-Au alloys required much longer annealing at these temperatures than did the Ag-Pd alloys, before the results indicated even fair homogeneity and isotropy. The longest time of annealing actually used was about 13 hours. The annealed condition is indicated by the letters RA.

In order to determine whether certain high values of a for condition R were due to distortion of the space-lattice by cold-working or to some other cause, the Ag-Pd alloys in condition A were rerolled after the x-ray examination so as to reduce the thickness by from 30 to 50 per cent. The increase in stiffness caused by this second rolling was very noticeable. The condition is indicated by the letters RAR. Finally, after examination in condition RAR, these same strips were reannealed and again examined. This final condition is indicated by the letters $RARA$.

Method of X-Ray Analysis.

The apparatus used has been fully described by Davey,[1] and only a brief statement to define the experimental conditions will here be given. The K-radiation of molybdenum, sufficiently isolated for photographic purposes by ZrO_2 filters, is allowed to fall, for from 8 to 20 hours on the

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[1] W. P. Davey, Opt. Soc. of Am. Jl., *5*, 479–493 (Nov., 1921).

face of a thin ribbon of the metal to be analyzed. The shadow cast by the edge of the ribbon, and the diffracted beams due to its suitably oriented crystals are caught by a strip of photographic film wrapped on a cylinder, the axis of which coincides with the edge of the ribbon. The current through the x-ray tube is about 30 milliamperes, the potential across it about 30,000 volts. The radius of the film (sensitive side) is $r = 20.36$ cm. for the particular film-holders here used.

The diffracted beams due to the individual crystals form full-sized images of the source,[1] which are separately distinguishable if the crystals are large enough, and which, when distinguishable, are more clearly defined the more homogeneous is the arrangement of atoms in the individual crystals. By keeping the sample at rest we thus gain information as to the dimensions of the crystals and their homogeneity. It should be mentioned that if the crystals are very large the images of the source are characteristically blurred at certain points, but this aperture effect is easily distinguishable from the general blurring of the spots due to imperfections in a smaller crystal. If the spots are numerous and intense, as in the present series of photographs, the more remote edges of the bands which they form on the photographic film are easily located within a couple of tenths of a millimeter, whether the individual spots are distinguishable or not.[2] The relative intensities of the bands will differ from the normal if the crystals are not oriented isotropically.[3] The distance from the edge of the shadow of the ribbon to the corresponding (more remote) edge of any band is $s = 2r\,\theta$, where θ is the grazing angle of incidence at which "reflection" takes place. The data, then, are the values of s, which range in these photographs from 6 to 30 cm. From these data the corresponding values of the perpendicular distance, d, between consecutive planes can be directly computed by the formula

$$ d = \frac{\lambda}{2}\csc\left(\frac{s}{2r}\right), $$

where λ is the wave-length of the x-rays. In order to reduce the labor of computation by this formula a table was constructed giving $\log_{10} d$ to four decimals for the argument s at every 0.01 cm. from 2.50 cm. to 30.00 cm. The value of λ_2 for the longer wave-length component of the $K\alpha$ doublet, 0.71212×10^8 cm., used in the construction of this table, was that given by Duane and Patterson.[4] The same table was used for the

[1] L. W. McKeehan, Frank. Inst. Jl., *194* (1922).

[2] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[3] M. Polanyi, Zs. f. Phys., *7*, 149–180 (Nov., 1921).

[4] W. Duane, Nat. Res. Counc. Bull., *1*, 383–408 (Nov., 1920): W. Duane and R. A. Patterson, Nat. Acad. Sci. Proc., *8*, 95–90 (May 15, 1922).

shorter wave-length component of the doublet, $\lambda_1 = 0.70783 \times 10^{-8}$ cm., when the doublet was resolved in the photographs, by subtracting a constant correction (0.0026) from the tabulated values of $\log_{10} d$.

The values of $\log_{10} d$ were computed in this way for every measured value of s. The indices of the corresponding planes (hkl) of the space-lattice were determined by inspection, the order and spacing of the bands being characteristic of the face-centered cubic space-lattice always found for the alloys here studied. The order of reflection is conveniently included in the indices h, k, l; e.g., the second order from the planes (210) is indicated by the symbol (420). An auxiliary table was computed which gives $\log_{10} a/d$ for the first 54 bands of a simple cubic space-lattice, 22 of which, having h, k, l all even or all odd, are also found in the pattern for a face-centered cubic space-lattice. With this notation the usual formula[1] becomes

$$\frac{a}{d} = \sqrt{h^2 + k^2 + l^2}.$$

Adding the corresponding tabular numbers gives $\log_{10} a$ which should be the same for all the bands. Table I. shows how nearly this condition is satisfied. The mean value of $\log_{10} a$ was taken without weighting the separate values, since the more remote bands, on account of their relative faintness, have larger absolute errors in s and yield only slightly better values of a than do the more intense bands nearer the shadow of the specimen. The first band of the pattern, which is very intense, was sometimes rejected, however, if the values of s were inaccurate on account of a poorly defined shadow. A poorly defined shadow may be due either to use of too thin a sample or to over-exposure and partial reversal of the unshaded area.

ACCURACY.

An example of the data and calculations from a single film is given in Table I., which is self-explanatory. From calculations of this kind it is apparent that the probable error in the value of a from a single experiment is low; it is estimated at about 1 part in 500. Examination of different samples presumably alike showed however that these may differ in the value of a by as much as one per cent., although generally agreeing much closer. The widest variations occurred in condition R. Such variation is not surprising, since the value of a is really determined for a sample of metal which originally occupied only about one cubic millimeter in the ingot. In conditions RA and $RARA$ it is thought that the agreement of results for different samples justifies the statement

[1] A. W. Hull, PHYS. REV., (2), *10*, 661–696 (Dec., 1917).

that a is known to 1 part in 300. The compositions of the alloys, as given in Table I., are subject to errors which it is difficult to estimate.

TABLE I.

Material : Ag: Pd₁				Condition : RA		Film No. 298
Relative Intensity.	Arc Length, s, in cm.	Due to $K\alpha_1$ or $K\alpha_2$.	log ($d \times 10^8$).		Miller Indices.	log ($a \times 10^8$).
10........	6.35	2	0.3603		111	0.5989
4........	7.34	2	0.2979		200	0.5989
6........	10.42	2	0.1482		220	0.5997
4........	12.28	2	0.0787		311	0.5994
4........	12.82	2	0.0606		222	0.6002
1........	14.86	1	9.9963		400	0.5984
4........	16.28	1	9.9586		331	0.5980
1........	16.34	2	9.9597		331	0.5991
3........	16.72	1	9.9477		420	0.5982
1........	16.79	2	0.9486		420	0.5991
3........	18.42	1	9.9083		422	0.5984
1........	18.53	2	9.9085		422	0.5986
3........	19.64	1	9.8825		$\left(\begin{matrix}333\\511\end{matrix}\right)$	0.5982
1........	19.75	2	9.8828		$\left(\begin{matrix}333\\511\end{matrix}\right)$	0.5985
1........	21.52	1	9.8462		440	0.5988
3........	22.65	1	9.8262		531	0.5982
1........	22.78	2	9.8266		531	0.5986
2........	22.99	1	9.8205		$\left(\begin{matrix}442\\600\end{matrix}\right)$	0.5987
1........	23.13	2	9.8207		$\left(\begin{matrix}442\\600\end{matrix}\right)$	0.5989
1........	24.41	1	9.7974		620	0.5984
1........	24.56	2	9.7977		620	0.5987
1........	25.45	1	9.7816		533	0.5983
1........	25.78	1	9.7768		622	0.5985

Mean value log ($a \times 10^8$) = 0.59873,
$a = 3.969 \times 10^{-8}$ cm.

Even in the silver-palladium series an error as great as two or three per cent., which is improbably high, would not affect the conclusions drawn from the results. Evidence is given below for the belief that the composition was not appreciably altered by annealing.

NUMERICAL RESULTS.

Table II. contains the values of a determined from the photographs, together with the densities computed for the most homogeneous condition examined. The values of a as a function of the atomic per cent. of silver

TABLE II.

Formula.	Atomic % Ag.	Values of $a \times 10^8$.				Computed Density.	
		R.	RA.	RAR.	RARA.	RA.	RARA.
Ag......	100	4.080[1]	4.080[1]			10.49	
Ag₄Au...	80	4.104	4.081[2]			11.93	
Ag₂Au₂..	60	4.112	4.126[2]			13.50	
AgAu ...	50	4.082	4.088[2]			14.74	
Ag₂Au₃..	40	4.091	4.114			15.31	
Ag₃Au₇..	30	4.072	4.122[2]			16.06	
AgAu₄...	20	4.082	4.079[2]			17.44	
AgAu₉...	10	4.096	4.084[2]			18.24	
Au......	0	4.075	4.075[1]			19.24	
Ag......	100	4.080[1]	4.080[1]			10.49	
Ag₉Pd...	90	4.090	4.056	4.053	4.055		10.67
Ag₃Pd...	75	4.075	4.037	4.014	4.020		10.93
Ag₃Pd₂..	60	4.023	4.001	3.992	4.004		11.08
AgPd ...	50	4.006	3.982	3.974	3.975		11.28
Ag₂Pd₃..	40	4.004	3.969	3.949	3.956		11.43
AgPd₃...	25	3.949	3.945	3.952	3.934		11.60
AgPd₉...	10	3.924	3.921	3.930	3.909		11.81
Pd......	0	3.900[1]	3.900[1]			11.87	

are also presented graphically in Fig. 1, for the conditions used in the computation of densities. In determining the mass to be ascribed to each unit of structure the value $N = 6.0594 \times 10^{23}$, as given by Birge,[3] and the 1921 atomic weights: Ag, 107.88; Au, 197.2; Pd, 106.7, were chosen. The densities for the pure metals: Ag, 10.49; Au, 19.24; Pd, 11.87, are within the range of values usually obtained, those for gold and silver being very close to the accepted values. The density of palladium has been a matter of some doubt, values from 11.40 to 12.16 having been reported. It is thought that the value given here is the most accurate yet obtained.

The previously published values for the space-lattice parameters of these three metals are due to Vegard [4, 5] and Hull.[6] Vegard's data has been recomputed using $\lambda = 0.614 \times 10^{-8}$ cm. for the mean wave-length of the $K\alpha$ radiation of rhodium[7] and gives for silver, $a = 4.11 \times 10^{-8}$ cm., and for gold, $a = 4.09 \times 10^{-8}$ cm. both slightly higher than the values here found. Hull's value for palladium, $a = 3.95 \times 10^{-8}$ cm. is also

[1] Mean of several concordant values, including both conditions, R and RA.
[2] Mean of two concordant values.
[3] R. T. Birge, PHYS. REV. (2), *14*, 361–368 (1919).
[4] L. Vegard, Phil. Mag., (6), *31*, 83–88 (1916). Ag.
[5] L. Vegard, Phil. Mag., (6), *32*, 65–95 (1916). Au.
[6] A. W. Hull, PHYS. REV., (2), *17*, 571–588 (1921).
[7] W. Duane, loc. cit.

higher than those here determined by the same method, but he states that the lines on the photograph which he obtained were rather faint and diffuse, which in the light of the present study suggests inhomo-

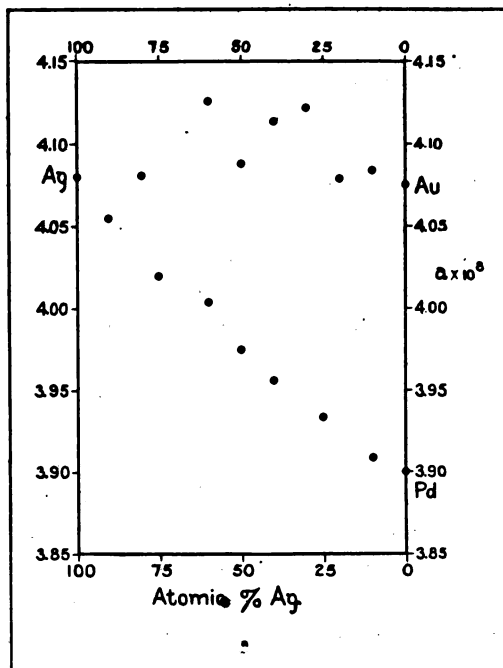
Fig. 1.

geneity. The presence of occluded hydrogen is a possible source of high values of a for this metal.[1]

QUALITATIVE RESULTS.

The variation in the parameter of the space-lattice is, to a first approximation, a linear function of the atomic per cent. of either component. There is, however, a tendency for the chemically unlike components, Ag and Pd, to be packed more closely than this, and a tendency for the components of widely differing mass, Ag and Au, to be packed less closely when mixed in certain proportions. Whether the correlation between the observed facts and the properties to which attention is invited by this choice of words is accidental or not cannot be determined from such meagre data.

The abnormally high values of a obtained for Ag_3Au_2, Ag_2Au_3, Ag_3Au_7 suggest that Tammann[2] is right in concluding that in the face-centered cubic arrangement of atoms solid solutions of the compositions A_3B,

[1] L. W. McKeehan, Amer. Phys. Soc. Washington Meeting, April, 1922.
[2] G. Tammann, Zs. f. anorg. u. allgem. Chem., 107, 1–239 (1919).

AB, AB_3 are particularly symmetrical and homogeneous. The compositions of the abnormal members of the Ag-Au series fall between these points, and the alloy Ag-Au appears to be normal in its value of a. The high value for the alloy Ag_3Pd_2 may be due to the same effect, but the distance of this point from the smooth curve hardly exceeds the probable error in its position.

It should be mentioned that the method of measurement favors low values of a at the expense of high values, so that what is actually determined is the smallest a (and the largest density) possessed by a considerable fraction of the crystals. The sag in the Ag-Pd curve might accordingly be attributed to a greater variability in a for the intermediate members. The reason for preferring the hypothesis of increased interatomic attraction is that the bands are no broader and no more diffuse for those members of the series which give low values of a than for those which give high values, and no wider than the width of the sample requires.[1] In fact it is for the highest points on the Ag-Au curve that the difficulty of determining a is most increased by diffuseness in the bands. It is perhaps not irrelevant that the excess of the melting point over the annealing temperature is least in the Ag-Au series, so that diffusion may be more effective here than in the Ag-Pd series in preventing regular arrangements, even if once established, from persisting.

Recent work by Bain[2] indicates that the gradual variation in crystal structure here found occurs in other solid solution alloys. He also obtained evidence, in the case of Cu-Ni and Cu-Au alloys, of the special regularity of distribution at the critical compositions, A_3B and AB_3, predicted by Tammann.[3] No such evidence was obtained in this study, perhaps because Ag and Pd have atomic numbers too nearly equal to give a "reflection" due to their difference and because these particular compositions were missing from the Ag-Au series.

The high values of a frequently found in condition R cannot be the immediate result of the cold-working which the material has suffered, for they do not recur in condition RAR. They are accordingly ascribed to inhomogeneity, existing in the original ingot, in the arrangement of atoms within each crystal, which does not permit the interatomic forces between unlike atoms to have their maximum effect. It will not suffice to suppose that different crystals have different compositions, for, as stated above, those with the more compact arrangements would be the ones for which a would actually be measured. After annealing, which renders the individual crystals more homogeneous, as proven by the

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[1] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[2] E. C. Bain, Min. and Met., Preprint 1139–N (Feb., 1922).

[3] G. Tammann, loc. cit.

better definition of the diffracted images of the source, the effect of cold-working is only to break up the existing homogeneous space-lattice into smaller units, and to shear and displace these fragments into less isotropic arrangements. The increase in intercrystalline area, and in the number of atoms thereon which do not fit into both the adjacent space-lattices, would account for the normal decrease in average density associated with cold-working where there is much shear. If working is so severe, however, that the space-lattice is destroyed throughout considerable volumes it is possible that some segregation of the components can occur at the same time. Subsequent crystallization may then leave the components less well mixed than before this severe working, and thus give rise to crystals with abnormal values of a. Some of the Ag-Au alloys were rolled until brittle, and in this condition gave hardly any evidence of crystalline structure, which would represent the end of the first stage in the supposed process. As noted above, recrystallization is particularly slow in the case of Ag-Au alloys, so that no attempt was made to reëstablish the crystal structure in these samples, especially since, if the supposed segregation exists, heating in this condition would change the composition by evaporation of silver.

The relative volatility of silver, mentioned in the last paragraph, is a possible source of error in the composition of the alloys, and this, particularly in the Ag-Pd series, might vitiate the conclusions as to the dependence of a upon the composition by changing the latter to an unknown extent. In order to estimate the possible effect of this volatility a sample of the alloy AgPd was repeatedly annealed at 870° C. for periods of 2 hours. No change in the value of a indicating a progressive change in composition could, however, be detected, so that any error due to this cause is negligible.

In conclusion I desire to express my indebtedness to my colleague Dr. E. F. Kingsbury, who placed at my disposal his first-hand knowledge of certain physical and chemical characteristics of the alloys here studied which suggested or confirmed the conclusions here presented.

THE CRYSTAL STRUCTURE OF IRON–NICKEL ALLOYS.

By L. W. McKeehan.

ABSTRACT.

Crystal structure and density of a complete series of pure iron-nickel alloys. —Fourteen alloys were prepared by melting together Armco iron and electrolytic nickel, then swaging the castings and drawing and rolling into thin tapes. X-ray diffraction patterns were obtained with these, after various heat treatments. With from zero to 25 per cent Ni, the structure is chiefly body-centered-cubic, the parameter a increasing from 2.872×10^{-8} cm for *pure iron* to about 2.89×10^{-8} cm. With from zero to 70 per cent Fe, the structure is chiefly face-centered-cubic, the parameter a increasing from 3.510 for *pure nickel* to about 3.60×10^{-8} cm. Around 30 per cent Ni, either structure is on the verge of instability and both or either may exist. Cold work tends slightly to increase the parameter. The densities of pure iron and nickel crystals come out 7.775 and 8.953 gm/cm³, respectively.

Speculations regarding atoms of iron and nickel. —It is probable that nickel atoms differ from iron atoms in possessing six electron orbits of a certain type in place of four. The behavior of these atoms in forming crystals is consistent with the idea that the directions of closest approach in either pure metal are the normals to the planes of these orbits and that in the intermediate directions, twelve for iron and eight for nickel, the atoms cannot approach so closely, these directions determining the positions of what we may call protuberances on the atoms. The electrons which are responsible for cohesion may be not the valence electrons but those in a deeper layer.

THE alloys of iron and nickel have long possessed great interest on account of the wide range in properties covered by the series and the irreversible character of certain of the transformations. No complete discussion of the alloys will here be attempted, only the results of X-ray crystal analysis being presented at this time. The method has been fully explained elsewhere, in connection with the analysis of certain alloys of silver with gold and palladium.[1] It should be stated here, however, that the experimental work on the nickel-iron series was practically completed before that on the noble metal series was commenced. The accuracy attained was not quite as high, partly on this account and partly on account of the more frequent occurrence of relatively large grains giving discrete spots in the film.

The qualitative work of Miss Andrews,[2] who found a transition in structure in the neighborhood of Fe(75)–Ni(25), from the body-centered cubic arrangement characteristic of Fe to the face-centered cubic arrange-

[1] L. W. McKeehan, Phys. Rev., **19**, 537–538 (1922).
[2] Mary R. Andrews, Phys. Rev., **17**, 261; **18**, 245–254 (1921).

ment characteristic of Ni, is the only previous investigation in which a graded series of alloys reasonably free from impurities was used. In the present study the alloys used were made from Armco iron and electrolytic nickel melted together in a Northrup induction furnace, cast, swaged, drawn, and rolled into tape 0.015 cm thick. Chemical analyses of the castings showed that the desired compositions were nearly attained. For the X-ray analysis the tapes were further thinned by dipping in aqua regia, the best thickness being about 0.004 cm. This form of sample is well adapted to high accuracy where, as in the present case, large crystals do not occur.[1] Besides end members in this tape form, iron and nickel powders of high purity were available and were examined, packed in thin capillary glass tubes.

Three conditions were investigated for most of the samples; the first (1) was without preliminary heat treatment, the metal having been last previously passed several times through cold rolls; the second (2) was after a short anneal at 900°–950° C (except as noted) followed by slow cooling in the electric resistance furnace; and the third (3) was after a further heating to about 600° C followed by rapid cooling in air on a cold copper plate. A few of the samples were also analyzed in a fourth condition (4) obtained by chilling after (2) in liquid air for an hour or more. In Table I. are recorded the parameters a of the space lattices present, the per cent of nickel found by chemical analysis, the mean distance between the nearest atom-centers and the density ρ, computed by means of the following constants:[2]

Atomic weight of Fe........................ 55.84
Atomic weight of Ni........................ 58.68
Number of molecules per gram-molecule....... 6.0594×10^{23}
Wave-length of molybdenum $K\alpha_1$........... 0.70783×10^{-8} cm
$K\alpha_2$........... 0.71212×10^{-8} cm

The results are given graphically in Fig. 1, which shows the variation in the parameters with the atomic composition which is given in the fourth column of Table I.

The increase in the face-centered cubic space-lattice parameter of nickel due to substitution of iron is evident, although not nearly so striking as the corresponding increase in other cases since studied.[3] The increase in the body-centered cubic space-lattice of iron due to substitution of nickel is just appreciable in the short range of stability of this

[1] L. W. McKeehan, Frank. Inst. J., **193**, 231–242 (1922).

[2] L. W. McKeehan, Science **56**, 754 (Dec. 29, 1922).

[3] L. W. McKeehan, Phys. Rev., **19**, 537–538; **20**, 424 (1922). E. C. Bain, preprint No. 1139-N. Issued with Mining and Metallurgy (February, 1922); Chem. and Met. Eng. **28**, 21 (Jan. 3, 1923).

space-lattice. The parameter for iron agrees with that found by others,[1] but that for nickel is less.[2] In the latter connection it is easy to see that high values would result from most of the probable impurities. The interesting changes in crystal structure in alloys with about 30 per cent Ni were noted by Miss Andrews.[2] This region is one of great variability in space-lattice parameter, and two reasons are suggested for this fact.
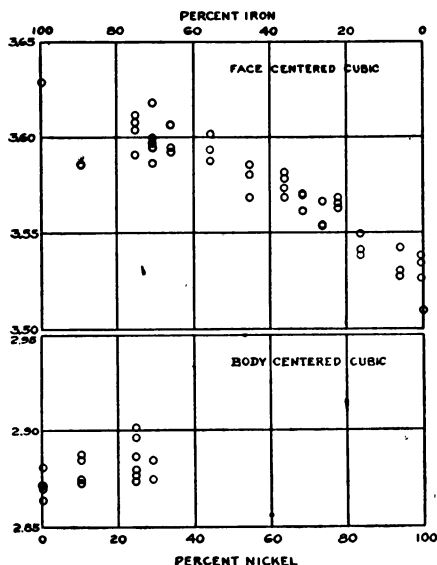

Fig. 1.

Either arrangement is on the verge of instability and correspondingly sensitive to small variations in composition or treatment, to the presence of impurities, and to similar causes. It is also possible for both phases to coexist, probably metastably, and there may be a certain degree of segregation of iron and nickel in such cases. The variability at the nickel end of the series may be attributed to impurities in the electrolytic nickel, which contained about half a per cent of other metals.

The general effect of cold-work is seen to be an increase of the parameters, due no doubt to incipient rupture in many of the crystals. The increase in crystal size due to annealing below the $A_3,(\alpha-\gamma)$ transformation is very apparent in the photographs. This transformation occurs over a very wide range in temperature in passing from pure iron to a little past 30 per cent Ni[3] and cannot be detected in these experiments at

[1] A. W. Hull, Phys. Rev., **10**, 661–696 (1917). A. Westgren, Nature, **109**, 817–818 (1922).

[2] A. W. Hull, Phys. Rev., **17**, 571–588 (1922).

[3] F. Hegg, Arch. des Sciences, **29**, 592–617; **30**, 15–45 (1910).

34 per cent Ni (atomic). Since positive errors are more probable than negative the lowest point in each vertical group is generally to be preferred.

The distances between adjacent atom-centers vary, of course, in the same way as the space-lattice parameters, but the small difference between the values obtained in the two types of space-lattice shows how nearly it is permissible to consider the atoms as spheres. While the idea is highly artificial it may be worth noting that the effect of diluting either pure metal with the other is the same as if the iron and nickel atoms were equal spheres, with, respectively, twelve and eight symmetrically distributed protuberances. In the body-centered cubic arrangement of such iron atoms, the protuberances would not lie on the lines joining adjacent atom-centers, and the parameter of the space-lattice

TABLE I.

Nominal Per Cent.		Actual Per Cent.	Atomic Per Cent.	Condition.	Body-centered cubic.			Face-centered cubic.			Note.
Fe.	Ni.	Ni.	Ni.		a.	$\frac{1}{2}a\sqrt{3}$.	ρ.	a.	$\frac{1}{2}a\sqrt{2}$.	ρ.	
100	0			2	2.872	2.488	7.775				(a)
100	0	0.15	0.14	1	2.881	2.495	7.704				(b)
				2	2.872	2.487	7.779				
				2	2.864	2.480	7.848	(3.629	2.566	7.712)	
				3	2.870	2.485	7.796				
90	10	10.68	10.20	1	2.885	2.498	7.718				(b)
				2	2.873	2.488	7.809	(3.586	2.536	8.034)	
				2	2.888	2.502	7.687				
				3	2.875	2.490	7.798				
75	25	25.85	24.91	1	2.897	2.509	7.676				
				2	(2.902	2.513	7.636)	3.591	2.539	8.062	(b)
				2	2.874	2.489	7.863	(3.608	2.552	7.944)	(b)
				2	2.880	2.494	7.816	(3.612	2.554	7.918)	(b, c)
				4	2.877	2.492	7.836	(3.604	2.549	7.966)	(b)
				4	2.887	2.501	7.752				
70	30	30.15	29.11	1				3.595	2.542	8.050	
				2				3.587	2.536	8.103	
				2				3.597	2.543	8.036	(c)
				4	2.875	2.490	7.868	(3.600	2.546	8.014)	(b)
				4	2.885	2.498	7.787	(3.618	2.558	7.898)	(b)
65	35	35.14	34.02	1				3.595	2.542	8.069	
				2				3.593	2.540	8.085	
				3				3.607	2.550	7.991	
55	45	45.57	44.35	1				3.602	2.547	8.063	
				2				3.588	2.537	8.163	
				3				3.594	2.542	8.117	

TABLE I (*continued*).

Nominal Per Cent.		Actual Per Cent. Ni.	Atomic Per Cent. Ni.	Condition.	Body-centered cubic.			Face-centered cubic.			Note.
Fe.	Ni.	Ni.	Ni.		$a.$	$\tfrac{1}{2}a\sqrt{3}.$	$\rho.$	$a.$	$\tfrac{1}{2}a\sqrt{2}.$	$\rho.$	
45	55	55.82	54.61	1				3.586	2.535	8.217	
				2				3.581	2.532	8.245	
				3				3.569	2.524	8.330	
35	65	64.82	63.70	1				3.569	2.524	8.371	
				1				3.574	2.527	8.335	
				2				3.582	2.533	8.279	
				3				3.579	2.531	8.301	
30	70	69.60	68.54	1				3.571	2.525	8.374	
				2				3.570	2.525	8.381	
				3				3.562	2.519	8.441	
25	75	74.51	73.76	1				3.567	2.522	8.424	
				2				3.555	2.514	8.510	
				3				3.554	2.513	8.508	
21	79	78.54	77.69	1				3.569	2.524	8.429	
				2				3.566	2.522	8.446	
				3				3.564	2.520	8.465	
15	85	84.48	83.83	1				3.550	2.511	8.586	
				2				3.542	2.505	8.647	
				3				3.539	2.502	8.672	
5	95	94.24	93.96	1				3.531	2.497	8.774	
				2				3.543	2.505	8.682	
				3				3.528	2.495	8.795	
0	100	99.50	99.47	1				3.539	2.503	8.736	
				2				3.527	2.494	8.824	
				3				3.535	2.500	8.765	
0	100			2				3.510	2.482	8.953	(a)

Notes: (a) Pure powdered metals, glowed in reducing atmosphere.
      (b) Values in parentheses due to few and faint lines.
      (c) Annealing temperature 700° C in place of 900°–950° C.

would be the same as if the protuberances did not exist, but nickel atoms substituted for any of the iron atoms must present protuberances to some or all of its neighbors and thus distend the space-lattice. The same argument would explain the effect of iron atoms upon the space-lattice of nickel, and the effect would here be more positive because the packing is already closer, with less room for interatomic adjustment. The atomic number of iron is 26, that of nickel 28, so that there are two more electrons in the latter than in the former. If the crystal is held together by forces acting along the lines joining adjacent atoms, it is perhaps per-

missible to regard the eight neighbors of each iron atom as attracted by the eight faces of four elliptical electronic orbits, and the twelve neighbors of each nickel atom by the twelve faces of six elliptical electronic orbits. The twelve symmetrically arranged directions farthest from the eight bonds in the case of iron, the eight symmetrically arranged directions farthest from the twelve bonds in the case of nickel would correspond to the protuberances in the more mechanical picture first suggested.

It is suggested that the electrons responsible for the cohesion of metallic crystals are not the so-called valence electrons but those of a deeper layer relatively more firmly attached to the nucleus, the external electrons being left free in the sense required for electrical conductivity. We are already accustomed to the idea that nominally external electrons may penetrate into nominally internal layers so this idea is not at all revolutionary. The comparative weakness of metal crystals would be a natural consequence of this less intimate connection between adjacent atoms which would thus form a transition stage between valence-held salt-like crystals and amorphous liquids.

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